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STRUCTURAL STUDIES OF TRANSITION METAL TO SILICON BONDING

by

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A THESIS

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled "STRUCTURAL STUDIES OF TRANSITION METAL TO SILICON BONDING" submitted by ROY SMITH in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

DEDICATION

To my wife

Abstract

A systematic structural study of the transition metal to silicon bond requires extensive investigation of systems of the type LM-SiXX'X'' where L is a group of ligands, M is a transition metal and X,X' and X'' are the silicon substituents. The structures described in this thesis were chosen to contribute to a comprehensive study of the effects of varying L,M,X,X' and X''.

The crystal structure of $(\underline{h}^5\text{-}C_5H_5)Re(CO)_2HSi(C_6H_5)_3$ was undertaken to investigate the effect of changing the transition metal while maintaining all other factors constant. The compound crystallises in the monoclinic system with spacegroup $P2_1/n$, unit cell dimensions a=13.161(12) Å, b=17.502(17) Å, c=9.579(4) Å, β=92.12(8)° and four molecules per unit cell. The rhenium compound is isomorphous with the manganese analogue, but certain differences in molecular structure are apparent. The rhenium-silicon bond is considerably shorter than the manganese-silicon bond when the different sizes of the metal atoms is taken into account.

The compound $(\underline{h}^5\text{-}C_5H_5)Fe(CO)H(SiF_2CH_3)_2$ crystallises in the orthorhombic spacegroup Pnam (# 62) with unit cell dimensions a=11.821(2) Å, b=7.157(2) Å, c=14.640(2) Å and four molecules in the unit cell. The molecular structure is compared with the structures of $(\underline{h}^5\text{-}C_5H_5)Fe(CO)H(SiCl_3)_2$ and $(\underline{h}^5\text{-}C_5H_5)Fe(CO)H(Si(CH_3)_2\text{-}C_6H_5)_2$. The geometry of the C_5H_5Fe structural fragment is constant

for all three molecules while the iron-silicon bond lengths vary in a manner that reflects the differences in electronegativity of the silicon substituents. The general trends in cis contacts between hydride ligands and silyl ligands appear consistent with repulsion rather than weak bond formation.

Two compounds which were believed to have empirical formula $Fe(CO)_4(Si(CH_3)_3)_2$ were studied. The first,which had been proposed as the dimeric species crystallises in the triclinic spacegroup $P\bar{1}$ with unit cell dimensions a=11.535(12) Å ,b=12.288(12) Å , c=12.543(12) Å ,α=72.01(6)^{o} ,β=87.31(8)^{o} ,γ=88.08(8)^{o} and two molecules in the unit cell. The true formulation of the compound was found to be $(CO)_3Fe(COSi(CH_3)_3)_4Fe(CO)_3$. Thus the molecule contains no iron-silicon bonds. The second compound was shown to be the authentic cis isomer of $Fe(CO)_4(Si(CH_3)_3)_2$ which crystallises in the orthorhombic spacegroup Pnam (# 62) with unit cell dimensions a=13.360(14) Å ,b=6.640(12) Å ,c=17.590(8) Å and four molecules per unit cell. The precision of the structure is limited by the disorder of approximately 6% of the molecules in the crystal.

Acknowledgement

The author wishes to express his gratitude and sincere appreciation to:

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My wife, Lian, for her patience.

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Chapter One

Introduction to Transition Metal to Silicon Bonding

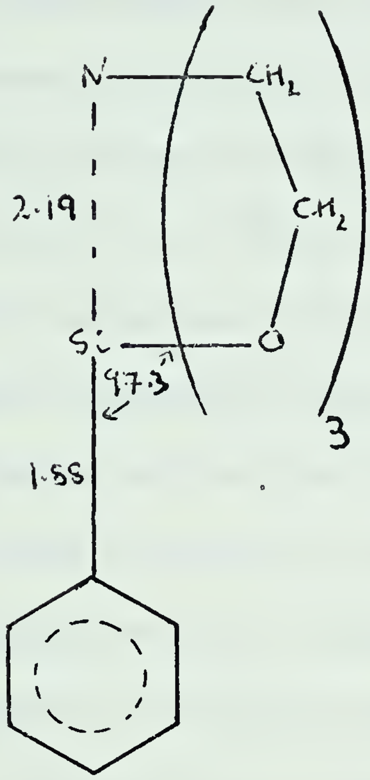
The stereochemistry of silicon in most of its compounds is based on the tetrahedron and the bonding to silicon in most of these cases can be explained in terms of interaction of ligand orbitals with silicon 3s and 3p orbitals only. However, in many molecules the bonding to silicon seems to involve an interaction between the empty 3d orbitals of silicon and the σ and π orbitals of adjacent atoms. Thus, the existence of penta-coordinated (as well as hexa-coordinated) silicon atoms, together with the partial double bond character of Si-O, Si-N, or Si-S bonds in siloxanes, silazanes or silthiazanes[1] and photoelectron spectra of methylchlorosilanes and related compounds[2,3], have suggested the participation of silicon 3d orbitals in the bonding of these compounds.

Crystal structures of several molecules containing penta-coordinated silicon have been reported showing that in these cases the favoured coordination geometry around silicon is that of a trigonal bipyramid. This particular geometry requires the participation of the silicon $3d_{z^2}$ orbital[4]. The detection of five coordination per se does not provide sufficient evidence to invoke the participation of the silicon 3d orbitals. For example, in 1 bromo-μ-trimethylsilyl pentaborane(9) the silicon atom has five close contacts, three to carbon atoms of methyl groups and two to boron atoms[5], and in this case the bonding in the $Si-B_2$ fragment is described in terms of a three centre two electron bond from a single silicon sp^3 hybrid and two boron orbitals.

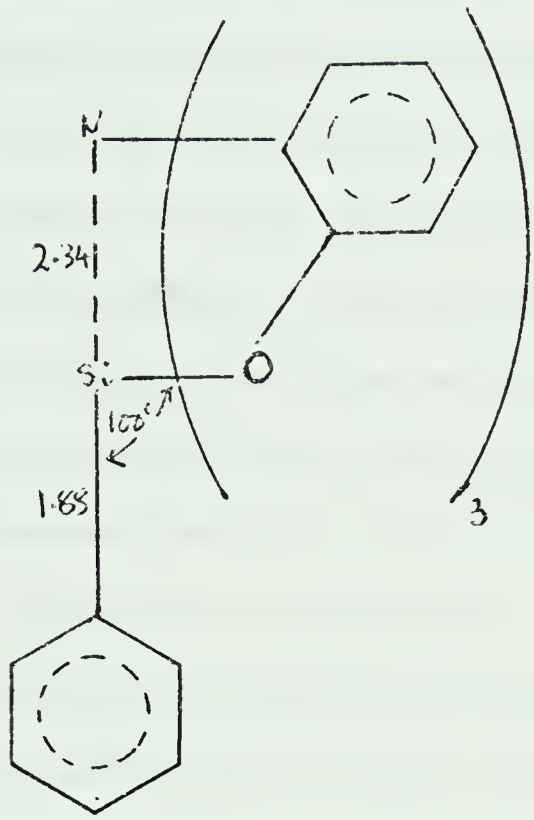
The penta-coordination of silicon has been claimed to exist in the in the silatranes[6-9]. The crystal structures of several silatranes show silicon with four nearest neighbours in a distorted tetrahedral array and with one relatively close contact to a nitrogen at a distance of the order of 2.12-2.34 Å. Major structural features of the molecules are shown in Figure (I) overleaf.

Figure(I)

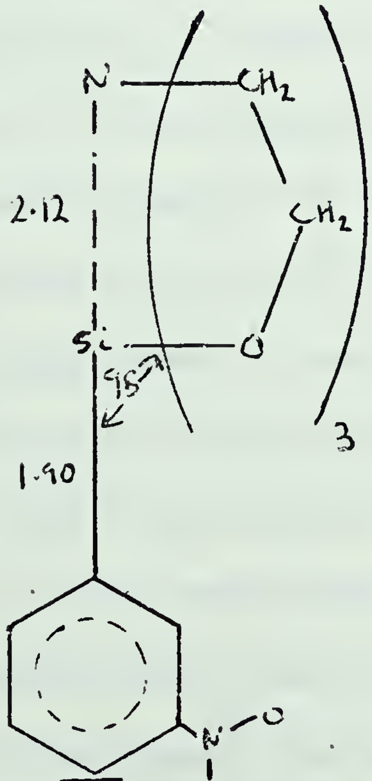
The major structural features of the silatranes



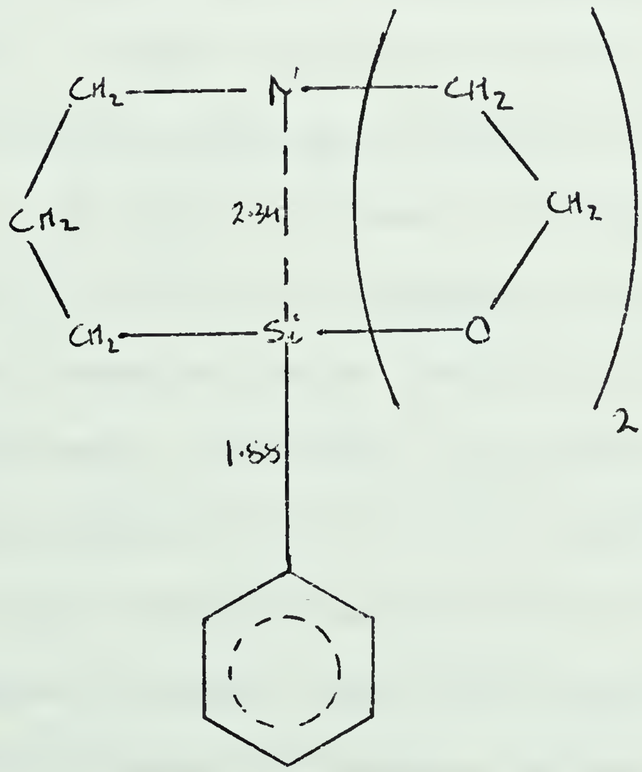
I



II



III



IV

The fifth and long contact has been considered to be bonding in nature but as the figure indicates a close approach to silicon by nitrogen is dictated by the fused ring structure. The silicon to nitrogen contacts in this series of compounds should be compared with the average Si-N distance of 1.98 Å which was found for $((CH_3)_2NSiH_3)_5$ (reference 10). In the latter structure the coordination about silicon appears to be a trigonal bipyramid with the nitrogen atoms in the apical positions. Assignment of hydrogen atoms in the equatorial positions, while reasonable from a structural point of view, could not be confirmed with certainty since the residual peaks in the electron density map were comparable to the noise level. Also the authors indicate that their data suffers from a systematic error since one silicon-nitrogen distance at 2.09 Å differs from the mean by more than five standard deviations. Nevertheless it can be seen that some of the silicon-nitrogen distances in the silatranes approach the values observed for similar distances in $((CH_3)_2NSiH_3)_5$, (reference 10). In these two cases (I and III in Figure (I)) the arguments for penta-coordination of silicon are more persuasive than for II and IV. The difference between silicon-nitrogen distances in I (2.19 Å) and III (2.12 Å) i.e. a response to a change in the <u>trans</u> ligand is particularly important to the deduction of the existence of a silicon-nitrogen bond. The changes in the ring structure in II and IV preclude any simple deduction of electronic effects in these cases. Nevertheless it seems reasonable to state that the weak nitrogen-silicon bond is enhanced by electro withdrawing groups on silicon if the ligand ring structure promotes (or, perhaps, allows) this bond formation.

In compounds in which a transition metal is bonded directly to silicon the coordination of silicon is best described as tetrahedral. In the few transition metal hydride species a close approach by the hydride ligand to the silicon atom lends to consideration of incipient five coordination, i.e. the case is somewhat similar to the silatrane species discussed previously. However, structural studies of these hydridic species were conducted concurrently with the work described in this thesis and discussion of these particular species is deferred to chapter three.

The major point of concern in discussing transition metal to silicon bonding has been the estimation of the extent to which the 3d orbitals of silicon interact with the d orbitals of the metal to give multiple bond character to the metal-silicon bond.

The simple approach of detecting π bonding <u>via</u> a comparison of observed bondlengths with values calculated from covalent radii encounters the following major obstacles:-

(a) estimation of a radius that is appropriate for the metal in organometallic molecules[11],

(b) estimation of bond contraction due to inductive effects when groups attached to silicon are highly electronegative[12],

(c) estimation of the variations in the s and p characters, and concomitant changes in effective radii, in M-Si and Si-X bonds (M=metal, X=H, F, CL, alkyl or aryl) due to significant deviations from an ideal tetrahedral geometry for silicon. Some structural data on $M-M'X_3$ systems (M=transition metal, M'=main group IV element) have been examined for evidence of multiple bonding[13]. In this paper MacDiarmid

et al., also present the results of extended Hückel molecular orbital calculations on $Co(CO)_4SiCl_3$ and $Co(CO)_4SiF_3$. These calculations suggest that the contribution to metal-silicon bonding is small, but significant, and that it results from two contributing effects, (1) metal d with silicon d overlap, $(d \rightarrow d)\pi$ and (II) metal d overlap with silicon sigma antibonding orbitals $(d \rightarrow \sigma^*)\pi$. The back donation to sigma antibonding orbitals has found considerable favour in explaining trends in spectroscopic and structural parameters when comparing transition metal-alkyl and transition metal fluoro alkyl derivatives. A final proposal by MacDiarmid et al., was concerned with the nature of the secondary interactions with cis carbonyl groups. The suggestion that these interactions were attractive was qualified by the admission that extended Hückel theory does not account for interligand repulsions. Yet the effect was proposed to explain the general distortion found in structures containing $Mn(CO)_5Y$ or $Co(CO)_5Y$ fragments in which the equatorial carbonyl groups bend away from the axial carbonyl group.

The low value of the contribution (approximately 8%) of metal to silicon $d\pi \rightarrow d\pi$ bonding to the total metal-silicon overlap in the molecules $Co(CO)_4SiF_3$ and $Co(CO)_4SiCl_3$ is probably acceptable to both those who believe in metal-silicon $d\pi \rightarrow d\pi$ bonding and to those who deny the importance of π bonding and propose that σ inductive effects dominate transition metal to silicon bonding[14]. Provided the metal-silicon $d\pi \rightarrow d\pi$ overlap is small the two views are not mutually exclusive. However, cobalt is a metal with particularly stable d orbitals and it must be recognised that for metals with less stable d orbitals, a better energy match between metal and silicon d orbitals might produce a more

substantial π component to the metal-silicon bond. A comparison of the structural features of analogous compounds of the first and second (or third) row transition elements should prove particularly informative in this respect.

A systematic study of transition metal to silicon bonding would then appear to require careful evaluation of related molecules of the type LMSiXX'X'' (where L is a group of ligands, M the transition metal and X,X' and X'' are the silicon substituents). The structural trends should be examined for effects of (I) changing M, with L, X, X' and X'' constant and (II) changing X, X' and X'' with M and L constant. In certain systems changing the components of L could prove useful in that a comparison of metal-silicon and metal-ligand bond distances might allow deductions concerning the _cis_ and _trans_ influences[15] of the various ligands.

This thesis is concerned with the structural determination of four compounds which were believed to contain transition metal-silicon bonds. These structural studies were performed using single crystal X-ray diffraction techniques. The theory and general experimental background are to be found in standard reference texts[16-19]. Specific details of equipment and crystallographic structure analysis programmes are given in Appendix (I).

Appendix (II) contains the description of the determination of the molecular and crystal structure of 3,4-benzocyclodeca-1,5-diyne which was undertaken to gain crystallographic experience in light-atom structures.

Appendix(III) contains the computer programme specifically written for the solution of the structure of 3,4-benzocyclodeca-1,5-diyne.

Chapter Two

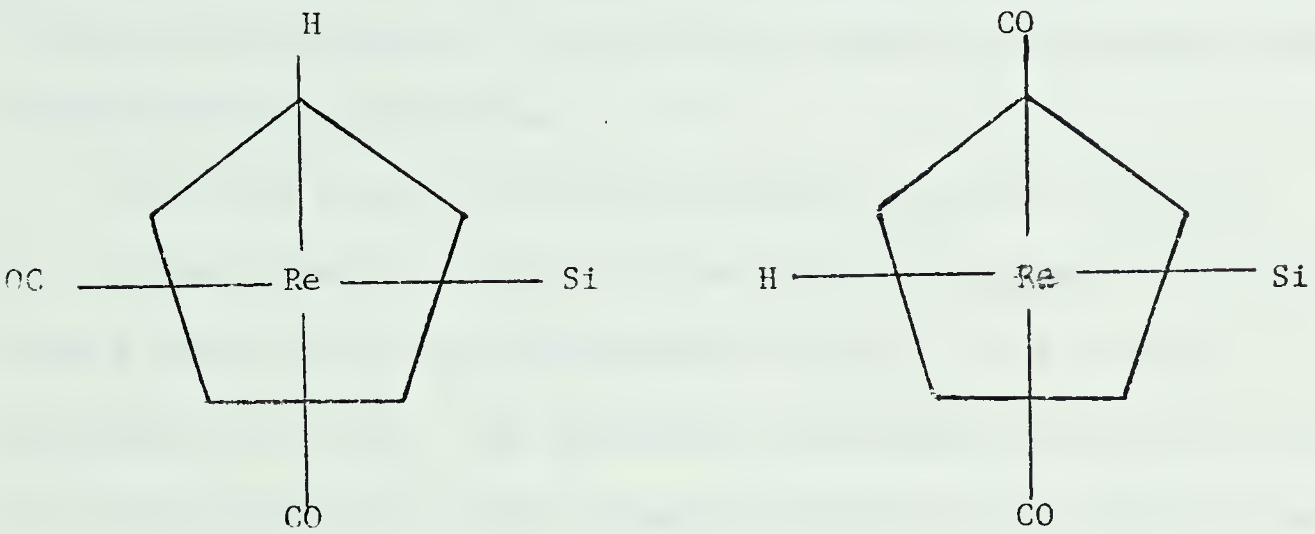
The crystal and molecular structure of *cis*-hydrido-triphenylsilyl (π-cyclopentadienyl) dicarbonyl rhenium.

Introduction

The structure determination of $(\underline{h}^5\text{-}C_5H_5)Re(CO)_2HSi(C_6H_5)_3$ was undertaken to investigate the effects of changing the transition metal in a related series of compounds. The structure of the comparable manganese compound $(\underline{h}^5\text{-}C_5H_5)Mn(CO)_2HSi(C_6H_5)_3$ is described elsewhere[20]. The rhenium and manganese compounds exhibit marked differences in stability in solution. The manganese compound dissociates readily (at room temperature) to give the highly reactive electron deficient $(\underline{h}^5\text{-}C_5H_5)Mn(CO)_2$ species and triphenyl silane while the rhenium compound requires elevated temperatures ($\sim 150^\circ C$) to give the equivalent reaction. For the rhenium system both '*cis*' and '*trans*' isomers appear to exist[21]. Figure (II) overleaf, clarifies the definition of '*cis*' and '*trans*' used for the study compound.

Figure(II)

The '<u>cis</u>' and '<u>trans</u>' isomers of $(\underline{h}^5\text{-}C_5H_5)Re(CO)_2HSi(C_6H_5)_3$



'<u>cis</u>'   '<u>trans</u>'

Only the <u>cis</u> isomer is isolated in a form suitable for X-ray diffraction studies. For the manganese compound there is no evidence for the 'trans' isomer.

<u>Experimental</u>

A sample of the compound was supplied by Dr. W.A.G. Graham and J. Hoyano and was recrystallised from a solvent mixture (methylene chloride and cyclohexane in approximately equal volumes). The symmetry of the diffraction pattern obtained from Weissenberg and precession photographs was found to be 2/m and the systematic absences

$$h\ o\ \ell \text{ for } h + \ell = 2n + 1$$

and

$$o\ k\ o \text{ for } k = 2n + 1$$

indicated the space group to be $P2_1/n$, a non-standard setting of $P2_1/c$ (no. 14). The general positions of $p2_1/n$ were derived as:-

$x,y,z;\ \bar{x},\bar{y},\bar{z};\ 1/2+x,\ 1/2-y,\ 1/2+z;\ 1/2-x,\ 1/2+y,\ 1/2-z$:

The facial development of the crystals, needed for subsequent corrections were determined to be

{-3,2,-3}; {1,0,-1}; {-1,0,1}; {0,1,0}; {0,-1,0}; {-1,0,1}:

A fresh crystal of external dimensions 0.15x0.30x0.35 mm was cleaved from a large crystal and mounted with the face {-1,0,1} normal to the goniometer head axis. The goniometer was placed on the diffractometer and the intensities of 2403 reflections with $0 < 2\theta < 42^{\circ}$ were measured. Molybdenum K_{α} X-radiation was used for these intensity measurements. The X-ray beam was made monochromatic by initial reflection from the 002 plane of a graphite crystal and the data were collected using the coupled $\omega/2\theta$ scan mode. A scan width of 2° in 2θ was employed with a scan rate of 2° per minute. The background was measured for 20 seconds on either side of the peak with the counter stationary. The intensity data were reduced to give structure amplitudes ($|F|$) after corrections for Lorentz, polarisation and absorption effects were applied assuming a linear interpolation of the background counts. The estimated standard deviations ($\sigma(|F|)$) were calculated from the expression of Doedens and Ibers[22] using a value of p=0.03 for p in the term that is not based on counting statistics. Only those data (1559 observations) which were considered significant by the criterion $I \geqslant 3\sigma(I)$ were corrected for absorption effects and used in the subsequent calculations such as structure refinement. The transmission factors for the study crystal ranged from 0.646 to 0.735 for Molybdenum K_{α} radiation (linear

absorption coefficient (μ) of $\sim$60 cm^{-1}).

Eleven intense non-axial reflections were carefully centred in 2θ on the Picker Four Circle manual diffractometer (no monochromator, CuK_{α_1} radiation, λ = 1.54051 Å) and these measurements used to refine the cell parameters and their standard deviations (in parenthesis)

$$a = 13.161(12)\ \text{Å}$$
$$b = 17.502(17)\ \text{Å}$$
$$c = 9.579(4)\ \text{Å}$$
$$\beta = 92.12(8)^{\circ}$$

The observed density, 1.69, was in acceptable agreement with the calculated density of 1.71, based on four formula weights per unit cell. Examination of the cell parameters and the intensities of the bulk of the reflections indicated that the rhenium compound was isomorphous with the manganese analogue.

Solution and Refinement of the Structure

The structure is isomorphous with the manganese analog[20] and the final coordinates of the manganese structure, with the exception of those of the proton of interest, were used as a trial structure for the rhenium compound. This solution proved adequate and the structure refined smoothly to R1 = 3.6% and R2 = 4.7%. The final standard deviation of an observation of unit weight was 1.25. The model and refinement details are briefly summarised. The function minimised was $\Sigma\omega(|Fo|-|kFc|)^2$;

$$\text{with } R1 = \frac{\Sigma(||Fo| - |Fc||)}{\Sigma|Fo|} \quad ; \quad R2 = \left(\frac{\Sigma(|Fo| - |kFc|)^2}{\Sigma\omega|Fo|^2} \right)^{1/2}$$

The scattering factors for Re, Si, O and C were obtained from Cromer's coefficients[23]. The scattering factors for the hydrogen were those of Mason and Robertson[24]. The real and imaginary terms of anomalous dispersion for Re and Si were included in structure factor calculations[25]. The model parameters were as follows: rhenium and silicon were treated as independent atoms and were allowed anistropic thermal parameters, the carbon and oxygen atoms of the carbonyl groups were treated as individual atoms but were constrained to isotropic thermal parameters the phenyl groups were treated as rigid bodies[26] with a carbon-carbon distance set at 1.39 Å and the carbon atoms of the cyclopentadienyl group were treated as a hindered rotor[27]. The hydrogen atoms associated were the phenyl and cyclopentadienyl rings were included at the calculated positions (assuming that they were coplanar with the carbon rings and that the C–H distance was 1.0 Å).

An electron density difference map computed using all of the data contained features of the magnitude ± 0.6 e/$Å^3$ (0.6 electrons per cubic Angstrom) in the vicinity of the rhenium atom. Elsewhere in the map the features were of the order of ± 0.3 e/$Å^3$. The second largest feature of this map was in a reasonable position for the one hydrogen atom omitted from the model (i.e. the hydrogen bound directly to the rhenium), but this alone does not provide sufficient evidence for the assignment of hydrogen to the peak, particularly when the peak is so close to a third transition series element and the largest residual peak is ignored.

A more rigorous assessment of the nature of the peak[28] involves the calculation of several electron density maps and changing the upper $\sin\theta/\lambda$ limit of the contributing data. Peak positions were determined using the method of Booth[29] and the results of this study are shown in Table (I) below.

Table (I)

A table of data from a series of electron density difference maps in cis $(h^5\text{-}C_5H_5)Re(Co)_2HSi(CoH_5)_3$

$\sin\theta/\lambda$ cut-off	x	y	z	Re-H dist.	Si-H dist.	C-H dist.	Observed Electron Density $e/\text{Å}^3$
0.20	0.014	0.255	0.031	1.73	2.17	2.17	0.16
0.25	0.005	0.258	0.036	1.62	2.20	2.05	0.26
0.30	0.005	0.265	0.028	1.66	2.29	1.99	0.35
0.35	0.005	0.260	0.011	1.68	2.02	2.12	0.38
all data	-0.001	0.272	-0.010	1.75	1.97	2.05	0.54

The peak that is most reasonably assigned to the hydride is found to be the largest feature in all maps with a maximum $\sin\theta/\lambda$ limit < 0.35. The largest peak of the all data map appears to arise from the high angle data and is more likely due to errors in the thermal parameters of the model. The inclusion of this hydrogen atom in the model

decreased R1 and R2 to 0.035 and 0.046 respectively. When the parameters of this hydrogen atom were allowed to vary in least squares refinement they stayed within one standard deviation of the coordinates obtained from the electron density maps[30]. The hydrogen can be assigned, tentatively, to a location approximately 1.7 Å from rhenium, and with non-bonded contacts to silicon and carbon of approximately 2.2 and 2.1 Å respectively.

Results

The observed and calculated structure amplitudes as obtained from the final cycle of least squares refinement are listed in Table (II), overleaf. Table (III) contains the final atomic parameters and their standard deviations for the independent atoms. The group parameters are collected in Table (IV) and the atomic coordinates derived from these group parameters are given in Table (V). Intermolecular contacts are normal for a molecular crystal and none are listed. Tables (VI) and (VII) list pertinent intramolecular angles and distances respectively. Tables (II) - (VII) follow, in order, after Table (II).

Following Table (VII) Figure (III) depicts a skeletal view of the core of the study compound seen down the vector from the rhenium atom to the centre of the cyclopentadienyl ring. Figure (IV) on the page thereafter shows the packing of several molecules seen perpendicular to the bc plane.

[illegible]

[illegible]

[illegible]

[illegible]

Table (II)

Structure Amplitudes (x10)

A comparison of Observed and Calculated Structure Amplitudes (x10)

for the molecule *cis* $(\underline{h}^5\text{-}C_5H_5)Re(CO)_2HSi(C_6H_5)_3$

Table (II) contains seven pages.

H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL
L = 0**				-4	6	1750	1825	0	12	909	872	-5	2	1100	1117
-12	0	858	865	-3	6	1149	1148	-8	13	615	618	-3	2	2062	2056
-10	0	741	733	-2	6	687	651	-6	13	725	745	-2	2	312	290
-8	0	1235	1248	-1	6	442	453	-5	13	655	676	-1	2	1132	1073
-6	0	1194	1161	0	6	2002	1977	-3	13	565	544	0	2	366	381
-4	0	1110	1136	-12	7	666	640	-2	13	770	765	1	2	2666	2561
-2	0	435	419	-10	7	648	639	-1	13	302	340	2	2	437	415
-12	1	738	715	-9	7	277	262	-7	14	602	577	3	2	477	503
-10	1	1076	1031	-8	7	796	760	-6	14	440	413	4	2	933	883
-8	1	822	803	-6	7	1513	1520	-5	14	265	236	5	2	2618	2689
-6	1	1566	1542	-5	7	684	731	-4	14	699	702	6	2	356	329
-5	1	405	362	-4	7	340	360	-1	14	365	354	7	2	568	595
-4	1	965	936	-3	7	267	326	0	14	642	677	8	2	475	478
-3	1	1184	1144	-2	7	1877	1888	-6	15	739	698	9	2	1153	1241
-2	1	3303	3450	-1	7	396	453	-5	15	537	538	11	2	349	365
-12	2	829	770	-10	8	814	793	-3	15	365	412	-11	3	1074	1112
-10	2	772	742	-8	8	1123	1085	-2	15	639	652	-9	3	897	922
-8	2	1320	1333	-7	8	290	390	-4	16	503	473	-7	3	1138	1116
-7	2	306	261	-6	8	548	553	-3	16	456	464	-5	3	1569	1553
-6	2	807	824	-5	8	250	270	-1	16	360	403	-4	3	397	397
-4	2	1953	1964	-4	8	1744	1773	0	16	575	616	-3	3	235	258
-3	2	416	320	-3	8	997	1005	-2	17	552	537	-2	3	190	136
-2	2	1175	1123	-2	8	320	335	-1	17	290	332	-1	3	2897	2860
-1	2	373	424	-1	8	394	303	**L = 1****				0	3	922	878
0	2	3590	3799	0	8	1467	1435	-13	0	908	945	1	3	1252	1213
-12	3	743	804	-10	9	620	640	-11	0	379	377	2	3	900	849
-10	3	1067	1039	-9	9	379	417	-9	0	1412	1451	3	3	2177	2219
-8	3	881	920	-8	9	760	675	-7	0	1173	1177	4	3	190	234
-6	3	1483	1515	-6	9	1308	1361	-5	0	1819	1782	5	3	364	326
-5	3	401	393	-5	9	872	900	-3	0	3536	3547	6	3	247	246
-4	3	610	585	-4	9	253	282	-1	0	1394	1391	7	3	2045	2069
-3	3	816	783	-3	9	404	379	1	0	3011	3054	11	3	971	953
-2	3	2776	2765	-2	9	1479	1483	3	0	454	456	-11	4	497	521
-1	3	683	740	-1	9	299	494	5	0	2406	2477	-10	4	352	352
-12	4	673	657	-10	10	654	648	7	0	901	912	-9	4	955	960
-10	4	885	861	-8	10	893	857	9	0	976	960	-8	4	252	236
-8	4	1352	1379	-7	10	660	637	11	0	329	412	-7	4	1120	1109
-6	4	520	516	-6	10	330	318	-11	1	1163	1168	-6	4	260	266
-5	4	300	310	-5	10	263	379	-9	1	817	874	-5	4	804	844
-4	4	1905	1894	-4	10	1516	1525	-8	1	296	321	-4	4	405	381
-3	4	665	662	-3	10	599	628	-7	1	1403	1374	-3	4	1340	1359
-2	4	201	175	-1	10	676	708	-5	1	1282	1286	-2	4	613	587
-1	4	624	625	0	10	1245	1194	-3	1	1445	1400	-1	4	1089	1018
0	4	1299	1264	-10	11	516	497	-2	1	160	231	0	4	1269	1218
-12	5	590	582	-9	11	263	276	-1	1	1961	1949	1	4	1604	1580
-11	5	321	335	-8	11	646	633	0	1	579	631	2	4	865	829
-10	5	849	846	-7	11	289	241	1	1	1615	1552	3	4	445	460
-8	5	765	770	-6	11	1094	1057	2	1	530	531	4	4	394	440
-6	5	1831	1831	-5	11	855	833	3	1	3512	3631	5	4	2423	2440
-4	5	640	590	-3	11	446	436	5	1	976	952	7	4	237	190
-2	5	2183	2212	-2	11	1077	1058	7	1	1201	1230	8	4	300	287
-1	5	939	916	-8	12	667	700	9	1	530	487	9	4	1386	1364
-12	6	478	465	-7	12	651	661	11	1	1071	1060	11	4	420	432
-10	6	907	860	-6	12	449	434	-13	2	870	872	-12	5	285	249
-9	6	268	226	-5	12	552	515	-11	2	431	420	-11	5	902	901
-8	6	1273	1254	-4	12	1036	1037	-10	2	263	289	-9	5	725	715
-7	6	324	330	-3	12	487	486	-9	2	1219	1216	-7	5	1101	1119
-6	6	567	558	-1	12	334	407	-7	2	1322	1323	-6	5	386	357

H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL
L = 1**				-2	8	467	516	8	11	331	273	-2	0	2166	2162
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-4	5	605	584	0	8	530	511	-9	12	405	447	2	0	2192	2147
-3	5	1190	1202	1	8	1788	1780	-7	12	510	517	4	0	861	850
-2	5	690	682	2	8	1075	990	-6	12	496	537	6	0	2022	2048
-1	5	1883	1890	4	8	562	615	-5	12	1073	1054	8	0	317	321
1	5	950	944	5	8	1318	1316	-3	12	1185	1142	10	0	1083	1065
2	5	808	803	6	8	591	599	-2	12	881	925	-12	1	287	231
3	5	2270	2229	7	8	242	246	1	12	1005	987	-10	1	1389	1376
4	5	649	655	8	8	559	538	5	12	882	885	-7	1	474	433
6	5	477	509	9	8	1105	1055	6	12	396	414	-6	1	1924	1949
7	5	1621	1632	11	8	338	369	8	12	403	397	-5	1	182	190
9	5	384	292	-11	9	738	752	9	12	738	733	-4	1	1466	1446
11	5	887	933	-9	9	309	341	-8	13	507	481	-3	1	1130	1110
-11	6	487	509	-8	9	607	575	-7	13	533	563	-2	1	1339	1293
-10	6	455	439	-7	9	1128	1075	-5	13	526	537	-1	1	1528	1471
-9	6	1018	992	-5	9	1258	1282	-4	13	795	805	0	1	2163	2140
-8	6	337	316	-4	9	400	435	-3	13	668	703	1	1	489	468
-7	6	795	758	-3	9	857	897	-2	13	264	278	2	1	526	517
-6	6	362	424	-1	9	1240	1244	-1	13	1121	1131	3	1	205	174
-5	6	1392	1377	0	9	857	846	0	13	652	623	4	1	1640	1638
-3	6	1698	1709	2	9	439	607	2	13	253	307	6	1	958	943
-2	6	568	560	3	9	1210	1240	3	13	829	824	8	1	1909	1991
-1	6	302	298	4	9	467	508	4	13	306	341	10	1	531	507
1	6	2189	2180	6	9	690	709	7	13	735	733	12	1	920	931
2	6	754	763	7	9	1201	1220	8	13	473	445	-12	2	905	943
3	6	440	431	10	9	416	431	-7	14	306	373	-11	2	304	317
4	6	823	813	11	9	687	685	-6	14	601	612	-8	2	1768	1813
5	6	1474	1528	-10	10	458	441	-5	14	489	564	-6	2	852	876
7	6	409	397	-9	10	826	806	-3	14	804	804	-4	2	1569	1550
8	6	483	490	-7	10	591	582	-2	14	630	660	-3	2	166	126
9	6	1297	1240	-6	10	501	513	0	14	307	362	-2	2	1938	1929
11	6	495	476	-5	10	1111	1151	1	14	667	675	-1	2	952	887
-11	7	865	856	-3	10	1244	1279	5	14	703	697	0	2	1873	1834
-9	7	474	430	-2	10	940	962	6	14	657	621	1	2	384	330
-8	7	611	613	-1	10	578	599	-5	15	414	403	2	2	1782	1730
-7	7	1084	1091	1	10	1419	1396	-4	15	672	696	3	2	785	783
-6	7	328	344	2	10	632	676	-3	15	437	485	4	2	1406	1392
-5	7	1392	1389	3	10	267	302	-2	15	494	246	5	2	355	322
-3	7	1101	1115	4	10	547	560	-1	15	781	775	6	2	1773	1850
-2	7	237	245	5	10	908	938	0	15	549	546	8	2	252	76
-1	7	1765	1754	6	10	474	425	2	15	420	406	9	2	331	344
0	7	687	674	8	10	422	411	3	15	614	684	10	2	1296	1311
1	7	502	563	9	10	828	823	4	15	384	347	-10	3	1260	1256
2	7	572	610	-9	11	305	291	-2	16	567	670	-9	3	400	382
3	7	2046	2052	-8	11	530	578	0	16	287	362	-8	3	662	677
4	7	662	694	-7	11	963	933	1	16	491	523	-7	3	643	649
6	7	668	702	-6	11	339	321	2	16	349	360	-6	3	1659	1640
7	7	1185	1204	-5	11	937	901	3	16	639	164	-4	3	1388	1417
9	7	312	245	-4	11	747	753	5	16	449	480	-2	3	1639	1639
11	7	869	865	-3	11	815	867	-1	17	427	403	-1	3	912	882
-11	8	332	283	-2	11	291	321	0	17	465	518	0	3	986	983
-10	8	495	484	-1	11	1110	1138	2	17	336	294	1	3	473	468
-9	8	1072	1023	0	11	728	740	**L = 2****				2	3	1289	1453
-7	8	629	610	3	11	820	837	-12	0	932	934	3	3	511	512
-6	8	476	510	4	11	528	527	-8	0	1962	1937	4	3	1791	1845
-5	8	1076	1108	6	11	250	232	-6	0	778	782	5	3	178	207
-3	8	1805	1625	7	11	934	900	-4	0	2038	1995	6	3	587	596

H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL
**L =		2****		-10	7	939	921	5	10	304	332	-3	15	868	826
8	3	1687	1721	-7	7	628	653	6	10	972	1001	-2	15	430	467
11	3	287	304	-6	7	1359	1361	7	10	362	381	1	15	658	610
12	3	672	666	-4	7	712	705	10	10	676	705	2	15	386	410
-12	4	973	907	-2	7	2042	2006	-9	11	295	354	4	15	613	594
-9	4	421	406	0	7	1993	1994	-7	11	384	361	5	15	300	431
-8	4	1348	1401	1	7	368	367	-6	11	747	794	-4	16	335	342
-6	4	937	938	2	7	824	870	-4	11	394	396	-1	16	859	801
-5	4	244	299	4	7	1470	1493	-3	11	715	667	0	16	332	370
-4	4	1682	1717	5	7	689	675	-2	11	1080	1099	2	16	528	535
-2	4	400	448	6	7	361	368	0	11	1073	1090	3	16	467	521
-1	4	369	380	7	7	443	465	1	11	922	943	0	17	319	263
0	4	1438	1387	8	7	1123	1112	2	11	357	477	1	17	630	596
1	4	415	393	9	7	282	296	3	11	565	554	**L =		3****	
2	4	1677	1639	11	7	374	339	4	11	1020	975	-11	0	841	868
3	4	553	531	-9	8	520	472	5	11	493	492	-9	0	479	451
4	4	1302	1279	-8	8	1043	1019	7	11	278	268	-7	0	1971	1942
6	4	1728	1767	-7	8	308	317	8	11	670	732	-5	0	725	735
7	4	283	340	-6	8	503	471	9	11	312	285	-3	0	3285	3342
8	4	268	228	-5	8	813	836	-9	12	319	308	-1	0	1463	1455
9	4	308	233	-4	8	1325	1338	-8	12	709	695	1	0	1222	1187
10	4	1297	1293	-2	8	1568	1526	-7	12	287	276	3	0	1432	1393
-10	5	1151	1175	-1	8	526	517	-5	12	385	381	5	0	897	858
-8	5	498	458	0	8	1475	1494	-4	12	978	974	7	0	937	943
-7	5	726	759	2	8	1470	1457	-2	12	684	671	9	0	1191	1199
-6	5	1246	1284	3	8	1137	1106	-1	12	711	721	11	0	959	973
-5	5	230	235	4	8	245	313	0	12	928	792	-11	1	518	487
-4	5	987	979	5	8	450	424	2	12	1206	1218	-9	1	1352	1323
-2	5	2420	2365	6	8	1220	1234	5	12	404	342	-5	1	2259	2297
-1	5	167	172	7	8	378	408	6	12	531	522	-4	1	415	447
0	5	1644	1606	9	8	308	293	7	12	309	388	-3	1	910	917
1	5	430	423	10	8	756	794	-8	13	301	221	-2	1	403	407
2	5	1077	1058	-10	9	759	735	-7	13	404	386	-1	1	2095	2077
3	5	409	394	-9	9	322	319	-6	13	883	902	0	1	202	217
4	5	1548	1557	-8	9	273	236	-4	13	331	338	1	1	1700	1684
5	5	727	756	-7	9	540	503	-3	13	734	738	3	1	1715	1693
6	5	341	398	-6	9	1060	1062	-2	13	918	915	4	1	346	314
8	5	1398	1385	-4	9	386	398	0	13	1015	994	5	1	1223	1222
11	5	320	337	-3	9	733	712	1	13	781	756	6	1	291	291
12	5	674	739	-2	9	834	909	2	13	420	425	7	1	918	934
-12	6	849	893	0	9	1557	1545	3	13	285	354	9	1	1387	1339
-9	6	366	397	1	9	745	726	4	13	668	737	-11	2	990	1003
-8	6	1092	1095	2	9	942	956	5	13	418	438	-9	2	447	393
-7	6	303	315	4	9	1192	1248	8	13	466	464	-7	2	1666	1674
-6	6	688	663	5	9	545	550	-7	14	345	305	-6	2	243	226
-5	6	749	726	7	9	376	390	-5	14	476	469	-5	2	376	381
-4	6	1432	1441	8	9	875	896	-4	14	507	543	-4	2	489	500
-2	6	1133	1131	-9	10	310	386	-2	14	391	396	-3	2	2733	2780
0	6	1525	1458	-8	10	810	829	-1	14	664	688	-2	2	415	382
2	6	1417	1432	-6	10	273	317	0	14	626	719	-1	2	767	764
3	6	538	566	-5	10	659	653	2	14	848	849	1	2	1457	1447
4	6	198	186	-4	10	1300	1330	3	14	789	738	3	2	1252	1246
5	6	212	218	-2	10	939	966	4	14	359	253	4	2	570	585
6	6	1713	1733	-1	10	724	705	6	14	432	455	5	2	1296	1337
7	6	390	387	0	10	926	943	7	14	342	329	6	2	329	348
8	6	328	279	2	10	1351	1342	-6	15	556	569	7	2	1134	1145
9	6	272	337	3	10	737	754	-5	15	276	230	8	2	286	284
10	6	952	884	4	10	318	322	-4	15	436	399	9	2	677	622

H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL
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11	2	1079	1132	3	6	1387	1397	-2	10	230	257	3	15	667	636
-11	3	357	353	5	6	761	790	-1	10	536	515	5	15	286	405
-9	3	1166	1180	6	6	270	247	0	10	794	782	-3	16	443	499
-8	3	391	380	7	6	1009	1016	1	10	1418	1437	-2	16	322	351
-6	3	416	455	8	6	401	422	3	10	1090	1074	-1	16	274	282
-5	3	2219	2266	9	6	563	515	4	10	563	594	0	16	552	570
-2	3	505	489	11	6	810	837	5	10	820	806	1	16	365	401
-1	3	1579	1568	-9	7	1113	1128	7	10	871	883	**L = 4****			
1	3	595	572	-8	7	324	281	8	10	301	370	-12	0	548	543
3	3	1305	1302	-6	7	305	313	-9	11	733	673	-10	0	930	952
4	3	350	352	-5	7	1633	1617	-8	11	525	563	-8	0	629	593
5	3	1338	1391	-4	7	703	721	-6	11	478	490	-6	0	2158	2193
6	3	365	362	-3	7	458	453	-5	11	702	711	-4	0	768	791
7	3	973	967	-2	7	425	409	-4	11	243	277	-2	0	2071	2116
9	3	1089	1097	-1	7	1586	1610	-3	11	260	318	0	0	451	495
-11	4	924	941	0	7	229	195	-2	11	875	848	2	0	2143	2082
-7	4	1374	1423	1	7	1078	1072	-1	11	1161	1139	4	0	800	800
-6	4	648	668	2	7	242	267	1	11	488	476	6	0	1218	1159
-4	4	513	507	3	7	1321	1311	2	11	849	860	8	0	392	388
-3	4	1752	1766	5	7	1196	1235	3	11	928	917	10	0	502	511
-2	4	306	257	6	7	600	597	5	11	999	1033	-12	1	692	713
-1	4	213	293	7	7	492	549	6	11	438	457	-10	1	591	570
1	4	1869	1829	9	7	806	813	7	11	348	376	-8	1	1118	1150
2	4	276	283	10	7	362	331	9	11	575	608	-6	1	626	637
3	4	1098	1188	-11	8	908	923	-8	12	273	296	-4	1	2168	2170
5	4	1126	1166	-8	8	310	272	-7	12	663	687	-3	1	569	554
6	4	254	257	-7	8	1132	1115	-4	12	385	386	0	1	2283	2312
7	4	1381	1447	-6	8	653	670	-3	12	802	800	1	1	308	308
8	4	456	485	-4	8	691	677	-2	12	270	290	2	1	1118	1137
9	4	475	487	-3	8	1329	1314	0	12	636	613	4	1	1515	1497
11	4	1045	1037	-2	8	380	317	1	12	1088	1055	6	1	769	751
-11	5	290	255	-1	8	940	939	3	12	592	617	8	1	865	874
-9	5	1168	1169	0	8	905	910	4	12	801	822	10	1	620	617
-8	5	447	488	1	8	1745	1763	5	12	437	470	-12	2	511	469
-7	5	274	212	3	8	1086	1101	7	12	677	673	-10	2	832	842
-6	5	390	387	4	8	411	424	8	12	411	412	-8	2	551	578
-5	5	1736	1727	5	8	667	700	-6	13	462	463	-6	2	1668	1645
-4	5	541	534	7	8	906	904	-5	13	809	807	-4	2	415	463
-3	5	959	938	8	8	318	341	-4	13	372	357	-3	2	376	348
-2	5	852	816	-9	9	895	913	-2	13	493	465	-2	2	2020	2053
-1	5	2138	2125	-8	9	660	662	-1	13	725	722	-1	2	328	302
1	5	762	762	-6	9	268	227	2	13	749	720	0	2	397	429
3	5	1294	1340	-5	9	811	834	3	13	648	660	1	2	389	396
5	5	1243	1238	-3	9	316	358	5	13	816	819	2	2	2090	2115
6	5	391	381	-2	9	798	780	6	13	588	592	4	2	931	922
7	5	723	708	-1	9	1445	1422	-4	14	344	307	5	2	290	302
9	5	939	964	1	9	711	739	-3	14	638	671	6	2	1209	1207
10	5	301	383	2	9	554	549	-2	14	407	413	7	2	222	119
11	5	303	276	3	9	1208	1266	0	14	571	575	8	2	679	701
-11	6	822	788	5	9	1070	1059	1	14	369	536	10	2	632	627
-10	6	277	251	6	9	434	425	3	14	402	452	-10	3	518	529
-7	6	1273	1301	7	9	447	440	4	14	586	589	-8	3	1086	1083
-6	6	678	698	9	9	700	758	5	14	351	448	-6	3	376	382
-4	6	548	573	10	9	295	267	-5	15	564	565	-5	3	309	310
-3	6	1393	1411	-7	10	1027	991	-2	15	302	323	-4	3	1718	1729
-1	6	713	737	-6	10	498	487	-1	15	491	498	-3	3	393	376
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H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL
L = 4**				-6	7	336	342	9	10	370	413	-6	1	243	158
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0	3	2105	2100	-4	7	1329	1315	-7	11	493	476	-3	1	1375	1362
2	3	691	700	-3	7	725	748	-5	11	419	373	-1	1	423	401
3	3	229	214	-2	7	302	246	-4	11	689	690	0	1	200	204
4	3	1622	1616	-1	7	596	578	-3	11	452	444	1	1	1865	1882
5	3	325	295	0	7	1570	1571	-1	11	660	659	2	1	229	283
6	3	853	899	1	7	509	475	0	11	943	916	3	1	310	309
8	3	1109	1122	2	7	434	417	1	11	365	404	5	1	1676	1688
10	3	645	674	3	7	597	625	4	11	1058	1042	7	1	593	593
-10	4	638	636	4	7	1180	1186	6	11	557	541	9	1	760	768
-8	4	423	422	6	7	637	648	7	11	390	451	-11	2	704	754
-6	4	1294	1307	7	7	311	289	8	11	457	467	-9	2	819	809
-5	4	317	288	8	7	630	642	-6	12	762	719	-7	2	683	669
-4	4	440	434	10	7	670	672	-5	12	514	512	-5	2	1173	1173
-2	4	2042	2050	-10	8	784	760	-3	12	367	319	-4	2	329	330
-1	4	645	631	-9	8	342	368	-2	12	805	781	-3	2	745	765
0	4	296	306	-8	8	691	663	-1	12	327	343	-1	2	1815	1860
1	4	375	378	-6	8	1177	1146	1	12	417	472	0	2	352	313
2	4	1760	1743	-5	8	431	425	2	12	851	868	1	2	466	461
4	4	838	837	-4	8	240	213	3	12	372	437	2	2	609	610
6	4	1294	1367	-3	8	760	688	5	12	392	430	3	2	1769	1787
8	4	937	931	-2	8	1261	1320	6	12	707	716	5	2	599	604
10	4	715	703	-1	8	620	621	-7	13	436	454	7	2	1219	1197
-10	5	498	487	1	8	791	777	-5	13	386	356	8	2	263	168
-8	5	1165	1167	2	8	1122	1100	-4	13	829	767	9	2	326	288
-7	5	265	237	4	8	490	545	-3	13	334	352	-11	3	595	629
-6	5	423	412	5	8	269	246	-1	13	287	251	-10	3	325	374
-4	5	1757	1815	6	8	1079	1054	0	13	591	644	-9	3	646	625
-3	5	754	725	8	8	683	666	1	13	474	449	-7	3	812	818
-1	5	562	561	9	8	342	372	3	13	496	519	-6	3	279	328
0	5	1892	1860	10	8	387	372	4	13	688	620	-5	3	891	913
1	5	190	120	-10	9	638	606	6	13	426	393	-3	3	1584	1587
2	5	417	408	-8	9	991	978	-3	14	281	293	-2	3	493	480
3	5	653	607	-7	9	375	364	-2	14	569	566	-1	3	773	755
4	5	1382	1445	-4	9	820	829	-1	14	327	284	1	3	2094	2103
5	5	221	213	-3	9	387	431	1	14	290	328	2	3	348	342
6	5	711	683	-1	9	810	825	2	14	622	652	4	3	446	466
8	5	899	891	0	9	1210	1243	3	14	277	320	5	3	1553	1541
10	5	670	631	1	9	340	330	5	14	640	629	7	3	418	429
11	5	331	354	3	9	569	575	-4	15	549	526	9	3	838	829
-11	6	274	163	4	9	1250	1254	0	15	672	655	-11	4	681	674
-10	6	632	689	6	9	650	669	1	15	326	373	-9	4	656	690
-8	6	650	595	7	9	308	349	3	15	557	557	-7	4	671	681
-6	6	1179	1215	8	9	527	556	**L = 5****				-6	4	273	276
-5	6	369	386	-9	10	315	363	-11	0	855	888	-5	4	1070	1090
-3	6	632	591	-8	10	383	384	-9	0	820	844	-3	4	810	828
-2	6	1826	1838	-6	10	1119	1090	-7	0	862	896	-1	4	1482	1498
-1	6	917	932	-5	10	703	709	-5	0	1105	1040	0	4	772	739
0	6	366	344	-3	10	456	460	-3	0	783	661	1	4	473	451
1	6	689	702	-2	10	978	993	-1	0	2111	2120	2	4	470	487
2	6	1336	1336	-1	10	267	227	3	0	1622	1628	3	4	1841	1855
5	6	246	232	1	10	683	652	5	0	493	454	5	4	314	275
6	6	1203	1212	2	10	1181	1163	7	0	1065	1023	6	4	352	370
8	6	859	896	4	10	338	316	9	0	374	393	7	4	1115	1099
10	6	660	655	5	10	303	311	-11	1	605	569	9	4	513	490
-10	7	518	559	6	10	753	742	-9	1	661	675	-10	5	286	278
-8	7	1113	1130	8	10	616	636	-7	1	921	926	-9	5	668	713

H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL
L = 5**				0	9	496	420	-8	1	1018	1063	-4	6	800	816
-7	5	1004	1013	1	9	997	1006	-6	1	738	764	-3	6	335	356
-5	5	973	965	2	9	474	426	-4	1	798	802	-2	6	741	737
-3	5	1367	1362	4	9	483	510	-2	1	1048	1058	0	6	1206	1180
-2	5	547	539	5	9	933	967	0	1	802	814	1	6	271	211
-1	5	510	567	7	9	301	298	2	1	1447	1452	2	6	577	527
1	5	1404	1375	8	9	329	287	4	1	327	298	4	6	1027	1073
2	5	596	565	-8	10	467	515	6	1	1325	1339	5	6	382	312
4	5	489	468	-7	10	698	719	-10	2	896	955	8	6	908	896
5	5	1235	1255	-5	10	970	956	-8	2	702	738	-8	7	735	738
9	5	861	849	-4	10	336	351	-6	2	1020	1058	-6	7	543	557
-9	6	555	549	-3	10	343	263	-4	2	670	658	-5	7	260	303
-8	6	359	356	-1	10	846	823	-2	2	935	979	-4	7	871	888
-7	6	785	789	0	10	529	485	0	2	1145	1156	-2	7	795	775
-5	6	1177	1171	2	10	526	533	2	2	571	549	-1	7	268	282
-4	6	356	336	3	10	827	812	4	2	1376	1431	0	7	567	584
-3	6	670	691	6	10	295	301	5	2	334	315	2	7	1104	1102
-1	6	1281	1287	7	10	662	644	7	2	307	295	3	7	471	494
0	6	730	735	-7	11	493	433	8	2	915	933	4	7	440	412
2	6	222	236	-6	11	480	493	-8	3	1149	1176	5	7	299	294
3	6	1468	1441	-5	11	479	488	-6	3	727	715	6	7	738	758
4	6	252	245	-3	11	920	906	-5	3	270	322	7	7	326	188
6	6	425	434	-2	11	417	423	-4	3	830	853	-8	8	336	315
7	6	1040	1055	0	11	381	397	-2	3	995	995	-7	8	349	387
9	6	415	415	1	11	769	761	0	3	977	1001	-6	8	819	808
-10	7	288	276	2	11	259	212	2	3	1269	1323	-4	8	645	625
-9	7	721	723	5	11	701	744	3	3	281	300	-3	8	314	348
-7	7	848	818	-5	12	807	796	4	3	490	485	-2	8	863	862
-6	7	262	244	-4	12	413	384	6	3	1200	1184	0	8	1132	1148
-5	7	682	705	-3	12	330	378	-10	4	740	825	1	8	319	288
-3	7	1424	1388	-1	12	852	838	-8	4	405	378	2	8	314	256
-2	7	682	649	0	12	433	455	-6	4	873	873	4	8	715	723
1	7	1081	1116	2	12	338	311	-4	4	600	608	5	8	348	333
2	7	608	631	3	12	638	602	-2	4	1090	1069	-8	9	582	571
4	7	594	601	6	12	510	470	-1	4	141	62	-6	9	398	414
5	7	996	978	-3	13	765	732	0	4	1160	1178	-5	9	442	395
7	7	251	132	-2	13	457	445	1	4	268	251	-4	9	958	970
8	7	372	367	0	13	372	365	2	4	626	696	-2	9	829	847
9	7	823	823	1	13	642	653	4	4	1259	1294	-1	9	465	436
-9	8	586	569	2	13	401	420	5	4	350	379	0	9	495	455
-8	8	427	369	5	13	482	443	7	4	356	402	2	9	1081	1096
-7	8	880	868	-4	14	518	501	8	4	969	985	3	9	370	371
-6	8	302	252	-2	14	325	280	-8	5	965	995	5	9	383	406
-5	8	1016	1033	-1	14	705	706	-6	5	690	673	6	9	697	724
-4	8	444	436	0	14	501	452	-5	5	351	397	7	9	296	269
-1	8	996	1008	2	14	263	206	-4	5	857	831	-7	10	328	367
0	8	564	600	3	14	516	505	-2	5	831	809	-6	10	632	623
2	8	364	363	**L = 6****				0	5	786	817	-4	10	474	480
3	8	1221	1232	-10	0	1180	1153	1	5	259	237	-3	10	441	480
6	8	353	375	-8	0	640	642	2	5	1072	1041	-2	10	807	825
7	8	861	853	-6	0	938	923	3	5	313	337	0	10	1024	1041
9	8	302	296	-4	0	1128	1141	4	5	401	372	1	10	481	465
-9	9	620	618	-2	0	526	584	5	5	268	205	4	10	630	594
-7	9	527	496	0	0	1318	1272	6	5	1091	1099	5	10	319	362
-6	9	486	470	2	0	642	653	9	5	277	282	-6	11	322	252
-5	9	769	742	4	0	1366	1371	-7	6	308	263	-5	11	418	503
-3	9	1133	1152	6	0	271	310	-6	6	919	906	-4	11	791	824
-2	9	488	426	8	0	1032	1016	-5	6	250	196	-2	11	794	807

H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL
L = 6**				7	3	832	824	-3	9	772	788	6	4	468	472
-1	11	324	320	8	3	270	268	-1	9	361	345	-6	5	762	747
0	11	347	352	-5	4	1216	1242	0	9	378	296	-5	5	422	417
2	11	789	768	-3	4	544	582	1	9	789	769	-3	5	301	302
3	11	497	493	-2	4	294	264	3	9	870	927	-2	5	1032	1055
-4	12	545	526	-1	4	922	913	4	9	357	266	0	5	320	210
-3	12	545	551	0	4	299	307	-5	10	666	672	1	5	344	335
-2	12	585	646	1	4	743	788	-2	10	298	334	2	5	857	862
0	12	638	620	3	4	815	846	-1	10	823	791	4	5	341	314
1	12	512	520	5	4	916	958	1	10	569	550	-5	6	310	242
3	12	284	370	7	4	372	349	2	10	323	308	-4	6	754	775
4	12	522	557	-7	5	802	830	3	10	546	486	-3	6	275	239
-2	13	580	572	-5	5	295	284	-3	11	683	657	-1	6	266	268
-1	13	534	559	-4	5	318	248	-2	11	320	304	0	6	961	920
0	13	337	350	-3	5	1073	1058	-1	11	432	421	2	6	477	432
2	13	459	431	-1	5	626	608	0	11	413	373	3	6	257	169
L = 7**				1	5	937	936	1	11	671	704	4	6	652	643
-9	0	1150	1121	3	5	751	716	3	11	634	624	-5	7	443	389
-5	0	1188	1163	5	5	546	558	**L = 8****				-3	7	396	382
-3	0	851	883	7	5	767	796	-4	0	1086	1142	-2	7	700	675
-1	0	818	816	-6	6	448	432	0	0	827	756	1	7	327	315
1	0	602	588	-5	6	856	874	2	0	424	444	2	7	779	777
3	0	864	856	-3	6	455	424	4	0	590	608	4	7	447	442
5	0	633	607	-2	6	410	396	6	0	405	330	-4	8	598	542
7	0	348	398	-1	6	880	871	-6	1	891	905	-3	8	281	325
-7	1	1308	1314	1	6	736	712	-4	1	295	121	-1	8	321	347
-5	1	391	370	3	6	777	737	-2	1	1173	1155	0	8	742	741
-3	1	988	995	5	6	901	926	0	1	548	593	3	8	327	263
-1	1	830	844	6	6	329	333	2	1	825	831	-2	9	545	559
1	1	779	800	7	6	358	284	4	1	365	384	1	9	275	323
3	1	648	680	-7	7	682	721	6	1	589	580	2	9	577	583
5	1	726	743	-4	7	430	399	-4	2	1119	1120	**L = 9****			
7	1	759	799	-3	7	893	921	0	2	1056	1078	-3	0	699	693
-9	2	883	904	-1	7	455	442	2	2	375	457	-1	0	284	304
-5	2	1238	1239	0	7	407	416	4	2	677	678	1	0	994	926
-3	2	716	764	1	7	798	797	6	2	433	437	3	0	277	192
-1	2	832	874	3	7	772	766	-6	3	768	754	-3	1	273	253
1	2	641	656	4	7	269	260	-2	3	1294	1328	-1	1	922	941
3	2	860	842	5	7	421	413	0	3	497	480	3	1	928	936
5	2	728	754	-6	8	373	357	2	3	752	735	-3	2	761	721
7	2	379	339	-5	8	711	739	4	3	415	391	1	2	1087	1118
-7	3	1007	1002	-2	8	329	272	6	3	674	611	-3	3	363	312
-5	3	420	390	-1	8	823	810	-6	4	298	218	-1	3	826	812
-4	3	257	210	1	8	574	519	-4	4	962	981	3	3	860	839
-3	3	1025	1035	2	8	264	286	0	4	1217	1217	-3	4	798	803
-1	3	687	660	3	8	569	537	2	4	511	531	-2	4	299	287
1	3	941	910	5	8	837	813	3	4	287	223	1	4	943	963
3	3	834	887	6	8	377	315	4	4	726	717	-1	5	822	769
5	3	521	513	-4	9	391	397								

Table (III)

Independent Atom Parameters for cis ($\underline{h}^5$-C_5H_5)$Re(CO)_2HSi(C_6H_5)_3$

Anisotropic Atoms

Atom	x	y	z
Re	-0.11317(3)	0.24026(2)	0.06814(5)
Si	-0.04600(9)	0.20190(9)	-0.1600(3)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Re	0.035	0.045	0.041	0.0005	0.0025	0.0001
Si	0.038	0.038	0.040	-0.0004	0.0013	0.0023

Isotropic Atoms

Atom	x	y	z	U
C(1)	-0.082(1)	0.343(1)	0.113(1)	0.067(4)
O(1)	-0.058(1)	0.408(1)	0.138(1)	0.081(5)
C(2)	-0.209(1)	0.287(1)	-0.058(1)	0.054(4)
O(2)	-0.273(1)	0.311(1)	-0.136(1)	0.050(4)

The standard deviations of the above parameters are given in parenthesis and refer to the last digit reported.

Table (IV)

Group Parameters for cis $(\underline{h}^5\text{-}C_5H_5)Re(CO)_2HSi(C_6H_5)_3$

Rigid Bodies — Positional Parameters

Ring No.	X	Y	Z	D	E	F
1	-0.2189(4)	0.0925(3)	-0.3226(5)	3.33(1)	2.46(1)	4.81(1)
2	0.0126(3)	0.3405(3)	-0.3760(5)	3.20(1)	1.24(1)	3.39(1)
3	0.1721(4)	0.1059(2)	-0.1380(6)	2.27(1)	2.45(1)	3.39(1)

Hydrogen Rings

4 all parameters as for ring 1

5 all parameters as for ring 2

6 all parameters as for ring 3

Thermal Parameters

Ring No.	B1	B2	B3	B4	B5	B6
1	4.0(2)	5.9(3)	6.4(4)	6.1(3)	4.9(3)	3.5(2)
2	4.0(2)	4.7(3)	4.3(3)	4.5(3)	3.8(2)	2.8(2)
3	4.8(3)	5.3(3)	5.6(3)	5.5(3)	5.5(3)	4.1(3)
4	4.3	6.5	7.0	6.7	5.4	-
5	4.4	5.0	4.7	4.9	4.2	-
6	5.6	5.8	6.1	5.9	4.4	-

Hindered Rotors

Rotor no.	X	Y	Z	B	Bd	Radius
1	-0.1404(4)	0.1607(3)	0.2029(6)	4.3(2)	3.0(5)	1.226(6)
2	-0.1392(33)	0.1675(24)	0.1996(45)	2.5(14)	3.5(20)	2.16(4)

	D	E	F
1	2.32(1)	2.87(1)	2.49(1)
2	constrained to be as above.		

The standard deviations of the above parameters are given in parenthesis and refer to the last digit reported.

Table (V)

Parameters derived from groups in ($\underline{h}^5$-C_5H_5)$Re(CO)_2HSi(C_6H_5)_3$

Atom	x/a	y/b	z/c
C(21)	-0.2139(7)	0.1702(3)	-0.3524(9)
C(22)	-0.2884(6)	0.1250(5)	-0.4185(7)
C(23)	-0.2934(6)	0.0473(4)	-0.3884(7)
C(24)	-0.2239(7)	0.0148(3)	-0.2928(9)
C(25)	-0.1494(6)	0.0599(5)	-0.2270(7)
C(26)	-0.1444(6)	0.1376(5)	-0.2568(7)
C(31)	-0.0197(6)	0.3596(4)	-0.2437(5)
C(32)	0.0085(6)	0.4167(3)	-0.3357(7)
C(33)	0.0409(6)	0.3975(4)	-0.4679(7)
C(34)	0.0451(6)	0.3213(4)	-0.5081(6)
C(35)	0.0168(6)	0.2641(3)	-0.4161(7)
C(36)	-0.0155(6)	0.2833(4)	-0.2839(6)
C(41)	0.1041(9)	0.0946(5)	-0.2509(9)
C(42)	0.1975(9)	0.0571(4)	-0.2509(9)
C(43)	0.2654(9)	0.0684(5)	-0.1330(8)
C(44)	0.2400(9)	0.1172(5)	-0.0249(9)
C(45)	0.1467(9)	0.1574(4)	-0.0299(9)
C(46)	0.0787(9)	0.1434(5)	-0.1429(8)
H(21)	-0.2103	0.2263	-0.3741
H(22)	-0.3385	0.1484	-0.4874
H(23)	-0.3471	0.0146	-0.2710
H(24)	-0.2275	-0.0413	-0.2710
H(25)	-0.0993	0.0365	-0.1578
H(31)	-0.0431	0.3734	-0.1482
H(32)	0.0054	0.4718	-0.3065
H(33)	0.0611	0.4388	-0.5341
H(34)	0.0683	0.3074	-0.6035
H(35)	0.0197	0.2090	-0.4452
H(41)	0.0551	0.0864	-0.3325
H(42)	0.2158	0.0218	-0.3238
H(43)	0.3327	0.0413	-0.1292
H(44)	0.2889	0.1254	0.0566
H(45)	0.1282	0.1900	0.0479
C(11)	-0.1382(9)	0.2072(5)	0.2981(9)
C(12)	-0.2266(9)	0.1853(6)	0.2151(9)
C(13)	-0.1959(9)	0.1294(5)	0.1152(9)
C(14)	-0.0886(9)	0.1167(5)	0.1365(8)
C(15)	-0.0529(9)	0.1649(6)	0.2496(9)

....Continued

Table (V) -Continued

Atom	x/a	y/b	z/c
H(11)	-0.135(3)	0.164(5)	0.368(4)
H(12)	-0.291(3)	0.211(2)	0.221(4)
H(13)	-0.237(3)	0.112(2)	0.045(5)
H(14)	-0.048(3)	0.090(2)	0.082(4)
H(15)	0.015(3)	0.175(2)	0.282(4)

The standard deviations for the above parameters are given in parenthesis and refer to the last digit quoted. The hydrogen atoms are labelled with the same number as the carbon atoms to which they are attached.

Table (VI)

Intramolecular Distances in $(\underline{h}^5\text{-}C_5H_5)Re(CO)_2HSi(C_6H_5)_3$

a) bonded

Atom 1	Atom 2	Distance
Re	Si	2.49(1)
Re	C(1)	1.87(1)
Re	C(2)	1.89(1)
Re	C(11)	2.32(1)
Re	C(12)	2.31(1)
Re	C(13)	2.30(1)
Re	C(14)	2.31(1)
Re	C(15)	2.32(2)
Si	C(26)	1.93(1)
Si	C(36)	1.91(1)
Si	C(46)	1.94(1)
C(11)	C(12)	1.44(1)
C(1)	O(1)	1.19(1)
C(2)	O(2)	1.16(1)
Re	H(1)	∿1.66

b) non-bonded

Atom 1	Atom 2	Distance
C(1)	C(2)	2.50(1)
Si	C(2)	2.82(1)
C(2)	H(1)	∿1.99
Si	H(1)	∿2.19

Table (VII)

Interatomic Angles in $(\underline{h}^5\text{-}C_5H_5)Re(CO)_2HSi(C_6H_5)_3$

Atom 1	Atom 2	Atom 3	Angle subtended by atoms 1 and 3 about atom 2
C(1)	Re	C(2)	83.5(5)
C(1)	Re	Si	112.9(4)
C(2)	Re	Si	78.8(4)
Re	Si	C(26)	109.5(3)
Re	Si	C(36)	115.1(3)
Re	Si	C(46)	113.8(3)
Cpd	Re	Si	116.7(5)
Cpd	Re	C(1)	125.4(5)
Re	C(1)	O(1)	177.0(9)
Re	C(2)	O(2)	175.8(9)

Figure(III)

A skeletal view of the core of the cis-hydridotriphenyl silyl(cyclopentadienyl) dicarbonyl rhenium molecule seen down the vector from the rhenium atom to the centre of the C_5 ring

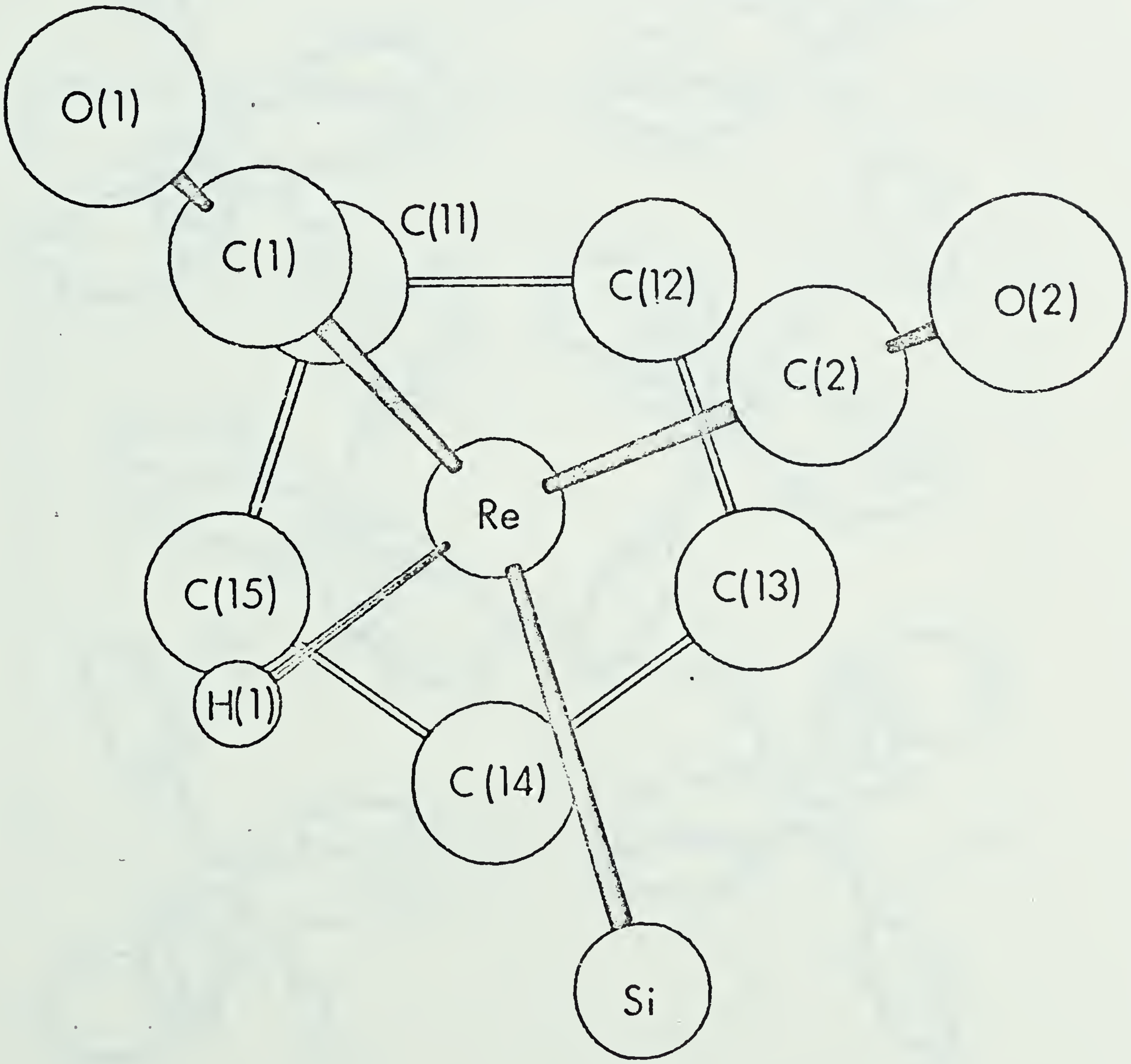
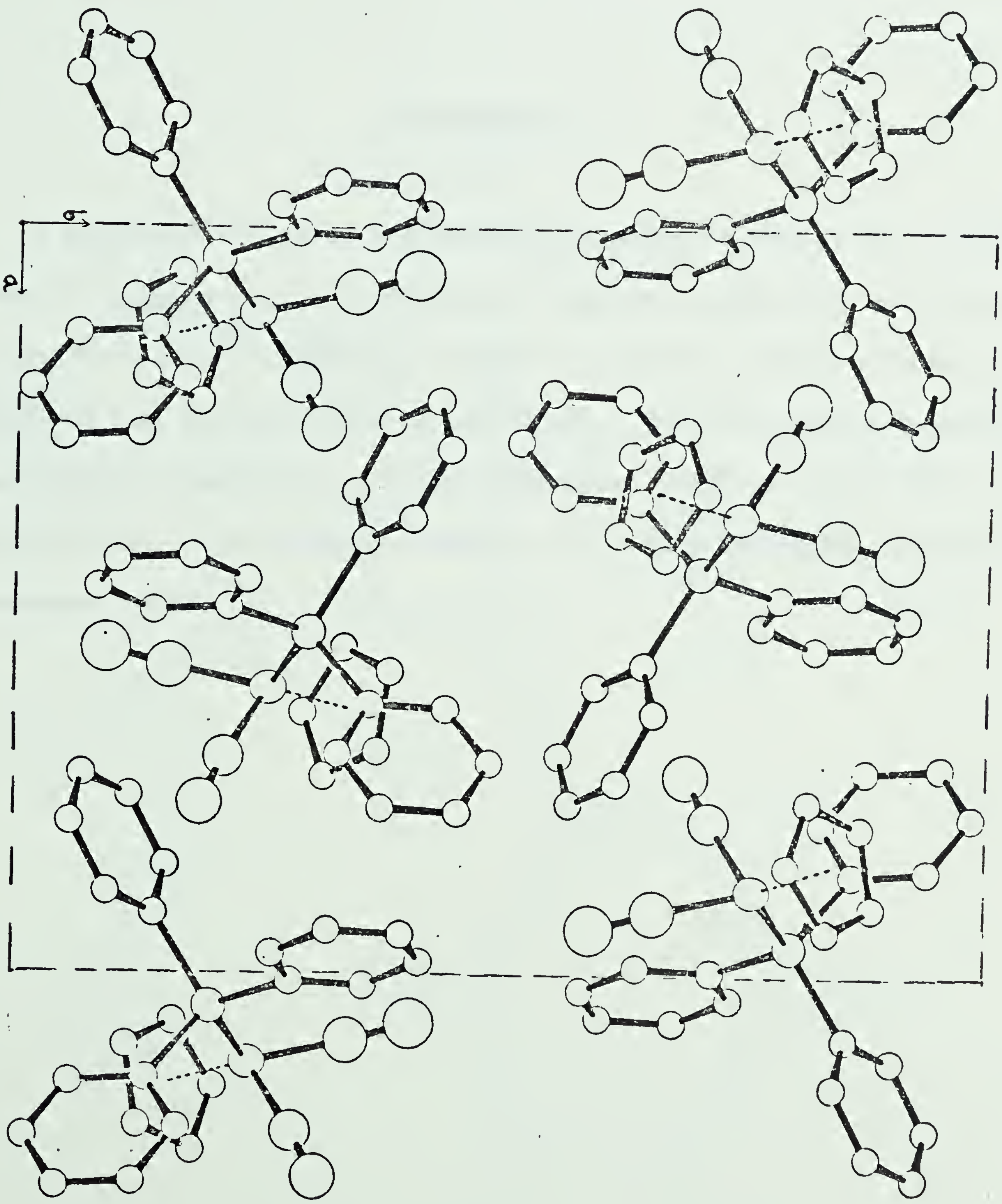


Figure (IV)

A packing diagram of cis-hydridotriphenylsilyl (cyclopentadienyl) dicarbonyl rhenium seen projected onto the ab plane

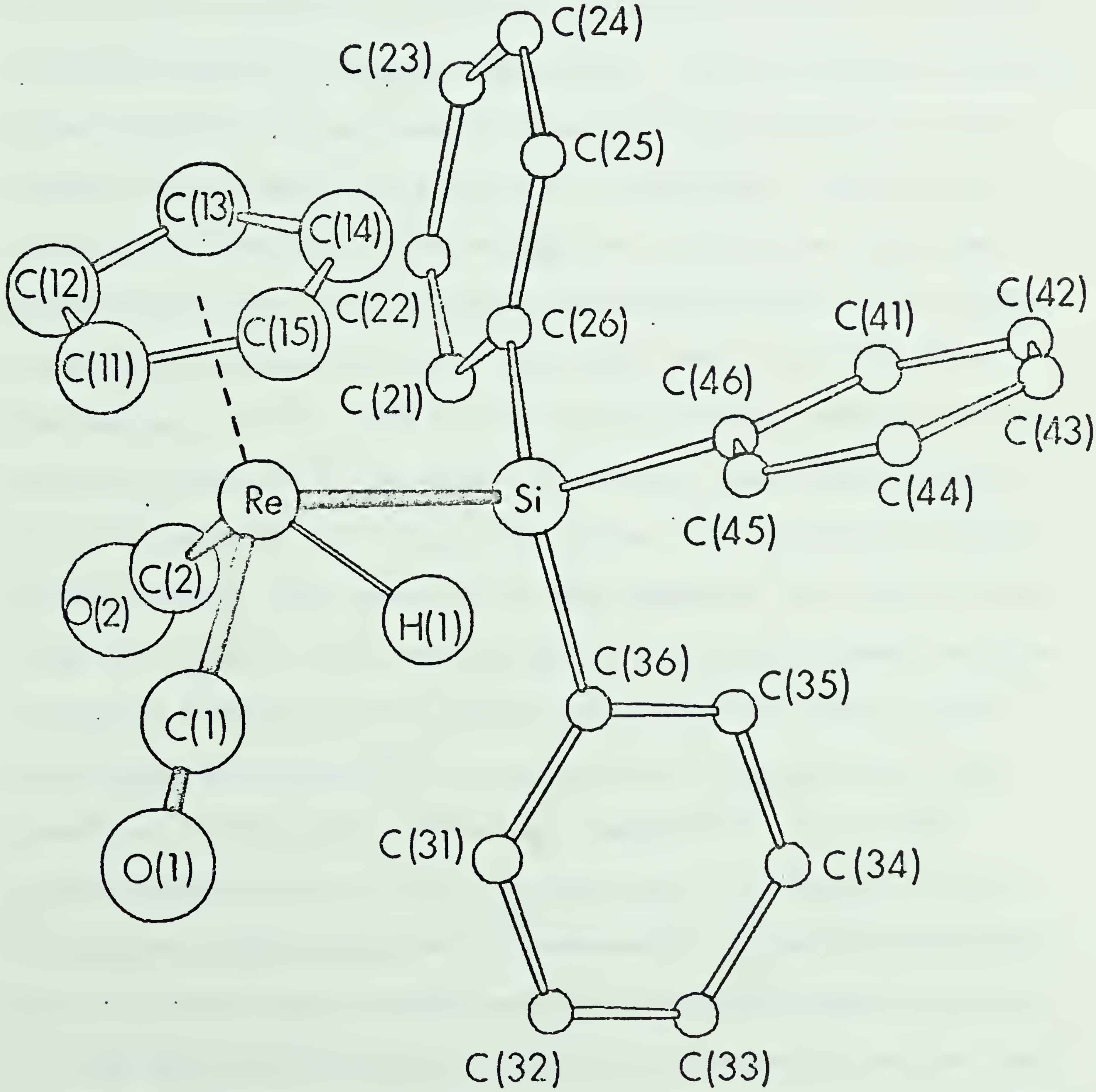


Discussion

A perspective view of the molecule is shown in Figure (V) overleaf. From the diagram little difference is apparent between the structures of the Re and Mn[20] compounds. However, while the structures are isomorphous they are not quite isostructural. The differences are small, but they are consistent with the significant differences in the positioning of the hydrogen bonded to the transition metal as will be discussed later.

Figure(V)

A perspective view of the cis-hydridotriphenylsilyl (cyclopentadienyl) dicarbonyl rhenium molecule.



The bond lengths in the $(\underline{h}^5\text{-}C_5H_5)Re(CO)_2$ fragment are normal by comparison with data from structures with similar structural components (see Table (VIII) overleaf). The distances from the rhenium atoms to the centres of gravity of the cyclopentadienyl rings exhibit a remarkable consistency at 1.95 $\pm$ 0.01 Å for the carbonyl derivatives indicating the relative insensitivity of the rhenium-cyclopentadienyl ring geometry to small changes in the trans ligand array. The only rhenium-cyclopentadienyl group[33] that shows a substantial deviation from the narrow range is $(\underline{h}^5\text{-}C_5H_5)Re(CH_3)_2C_6H_4CH_3$ (i.e. a non-carbonyl compound) and even in this case the difference might not be considered significant using conservative crystallographic statistical criteria. The rhenium to carbonyl distances in Table (VIII) range from 1.85 to 1.96 Å and the average value of 1.88 Å that is observed for this structure is towards the lower end of the range. The average carbon-oxygen distance is 1.17 Å which is at the higher end of the range observed in terminal carbonyl groups. The carbon-carbon bond lengths of the cyclopentadienyl ring are 1.44 Å, a value which appears to be in good agreement with the equivalent values obtained in other structures where either (1) the rotor model has been used[20], or (2) libration corrections have been made[38] or (3) librational effects are negligible[39]. The refined barrier height (3.0) for the C_5 hindered rotor corresponds to a root mean square angular libration of approximately 7.5° which is indicative of a relatively sharp potential well for a cyclopentadienyl derivative.

The rhenium-silicon bond at 2.49(1) Å is considerably shorter than the rhenium silicon bridge bonds of 2.54 Å as observed in $Re_2(CO)_8H_2Si(C_6H_5)_2$, $Re_2(CO)_8(Si(C_6H_5)_2)_2$, $Re_2(CO)_7H_2(Si(C_2H_5)_2)_2$ and $Re_2(CO)_6(Si$

Table (VIII)

A table of Re-cp[3], Re-C(cyclopentadienyl) and Re-C(carbonyl) distances in Å (standard deviations in parenthesis)

Compound	Re-cp distance	Re-C(C_5H_5) distance	Re-C(CO) distance	Reference number
$(\pi\text{-}C_5H_5)HRe(CO)_2Si(C_6H_5)_3$	1.96(1)	2.31(1)	1.88(1)	this work
$(\pi\text{-}C_5H_5)_2Re_2(CO)_5$	1.95(2)	2.29(1)	1.85(2)	31
$((CH_3)_3SiC_5H_4)Re(CO)_3$	1.95(2)	2.30(3)	1.86(4)	32
$(\pi\text{-}C_5H_5)Re(CH_3)_2C_6H_4CH_3$	1.89(2)	2.24(4)	-	33
$C_8H_9Re(CO)_3$	1.94(2)	2.28(3)	1.90(4)	34
$(C_6H_5)_2SiH_2Re_2(CO)_8$	-	-	1.95(6)	35
$HRe_2Mn(CO)_{14}$	-	-	1.95(3)	36
$Re_2(CO)_8[Si(C_6H_5)_2]_2$	-	-	1.94(2)	37
$Re_2(CO)_7H_2[Si(C_2H_5)_2]_2$	-	-	1.96(2)	37
$Re_2(CO)_6H_4[Si(C_2H_5)_2]_2$	-	-	1.96(2)	37

cp centroid of cyclopentadienyl ring

C_5H_5 cyclopentadienyl ligand

CO carbonyl

The standard deviations quoted refer to the last digit quoted.

$(C_2H_5)_2)_2$ (references 35, 37, 37 and 37 respectively). In contrast, for the manganese derivatives the manganese-silicon bond in $(\underline{h}^5\text{-}C_5H_5)Mn(CO)_2HSi(C_6H_5)_3$ (reference no. 20) is 2.424(2) which is longer than the bridging manganese-silicon bond length, 2.401(3) Å in $Mn_2(CO)_8(Si(C_6H_5)_2)_2$ (reference no. 41). The difference in effective covalent radii between manganese and rhenium can be estimated to be 0.17 Å from the different metal to cyclopentadienyl-carbon atom distances[42]. This empirical method is subject to criticism when used for the calculation of absolute values of covalent radii, but is useful for the evaluation of trends based on differences. The difference between manganese-silicon and rhenium-silicon bonds in the $M_2(CO)_8(Si(C_6H_5)_2)_2$ species is 0.14 Å (i.e. only 0.03 Å different from the covalent radius difference) whereas the corresponding difference in the $(\underline{h}^5\text{-}C_5H_5)M(CO)_2HSi(C_6H_5)_3$ species is only 0.09 Å. It is tempting to ascribe this difference in metal-silicon bonds to an enhanced π contribution to the metal-silicon bond for rhenium where the less stable d orbitals should be more effective in bonding to silicon 3d or σ antibonding orbitals. However, a marked difference in the apparent hydride location complicates the interpretation (<u>vide</u> <u>infra</u>).

The silicon to phenyl carbon bonds average 1.92 Å and are in a reasonable agreement to similar distances[20,35,43] observed in diphenyl silyl and triphenyl silyl derivatives of the transition metals. However all of these distances are longer than observed in simple aryl silanes (averaging 1.84 Å)[32]. Indeed, when silicon is attached to a transition metal, silicon to carbon(sp^2) bonds are longer than silicon to carbon (sp^3) bonds which is totally unexpected on the basis of the covalent

radii of carbon for the two hybridisation states (0.73 Å for sp^2 and 0.77 Å for sp^3)[24]. In $C_5H_4Si(CH_3)_3Re(CO)_3$ (reference no. 32) where the trimethyl silicon is a substituent of a cyclopentadienyl ring the expected trend in silicon-carbon distances is observed viz. Si-C(sp^3) 1.88 Å Si-C(sp^2) 1.83 Å. These values are the averages of the distances for the two independent molecules per assymetric unit and should be more reliable than indicated by the individual standard deviations of a single silicon-carbon bond (∿0.04 Å).

One expected effect of changing the transition metal (M) from rhenium to manganese in the compounds of the type $(\underline{h}^5\text{-}C_5H_5)M(CO)_2HSi(C_6H_5)_3$ would be a general reduction in interligand non-bonded repulsions due simply to the increase in size of the central metal atom and a concommitant increase in metal-ligand bond lengths. While this is generally true the non-bonded carbon-carbon contacts between the two carbonyl groups in each molecule are remarkably similar (2.50 Å for rhenium and 2.48 Å for manganese). This constancy of carbon-carbon contact coupled with the difference in metal-carbon distances results in a marked difference in (O)C-M-C(O) angles (83.5° for rhenium and 89.7° for manganese). The net effect of the angular and bond length changes in going from manganese to rhenium is to produce more space for the hydride ligand. The extremely short silicon-hydrogen contact (∿1.8 Å) in $(\underline{h}^5\text{-}C_5H_5)Mn(CO)_2HSi(C_6H_5)_3$ and $(\underline{h}^5\text{-}C_5H_5)Mn(CO)_2HSiCl_2C_6H_5$ (references 20 and 43 respectively) does not appear to be present in the rhenium compound.

Since the direct location of the hydride ligand is less certain in the case of $(\underline{h}^5\text{-}C_5H_5)Re(CO)_2HSi(C_6H_5)_3$ the possible positions for the hydride ligand were examined from the standpoint of minimising intra-

molecular non-bonded contacts. Three repulsive non-bonded contacts (C(1)....H, Si....H and H(45)....H) appear to be sensitive to the hydride location. Table (IX) overleaf contains these contacts calculated for a range of hydride positions using angular parameters. The angles (θ, ϕ) in this table are the conventional polar coordinates. The positive z direction (i.e. $\theta = 0$) was defined by the vector from the rhenium atom to the centre of the cyclopentadienyl ring, the Re-C(1) vector was defined as having $\phi = 0.0$, and the Re-H distance was assumed to be 1.68 Å, i.e. the distance found in structures containing rhenium-hydrogen bonds[36,44]. The data in Table (IX) show the definite trends;-

(1) for θ constant the C(I)....H contact increases with increasing ϕ while Si....H and H(45)....H contacts both decrease,

and (2) for ϕ constant the C(I)....H and Si....H contacts increase with increasing θ while the H(45)....H contact decreases.

Since all contacts in this table can be judged to be repulsive[45], an increase in the contact distance corresponds to a decrease in the repulsion. The position of the hydride ligand determined from the difference maps corresponds to $\phi = 85^{o}$ and $\theta = 115^{o}$, as predicted from Table (IX). This position seems to represent a reasonable minimum of the repulsions when the observed non-bonded contacts C....H[20] and H....H[46] are taken into consideration. A quantitative theoretical treatment is not feasible at this time since it would require a very accurate calculation of molecular energies.

The important structural differences between $(\underline{h}^5\text{-}C_5H_5)M(CO)_2HSi(C_6H_5)_3$ (M = Mn and Re) are concerned with the silicon to metal bond

Table (IX)

Hydride - other atom contacts for a series of hydride atom locations

$\theta = 120^o$

ϕ	75	80	85	90	95	100
C(1)-H	1.72	1.82	1.93	2.03	2.12	2.21
Si-H	2.45	2.34	2.22	2.10	1.98	1.85
H(45)-H	2.16	2.10	2.05	2.01	1.99	1.99

$\theta = 115^o$

ϕ	75	80	85	90	95	100
C(1)-H	1.78	1.89	1.99	2.10	2.18	2.28
Si-H	2.50	2.38	2.26	2.14	2.01	1.88
H(45)-H	2.07	2.00	1.94	1.91	1.88	1.88

$\theta = 110^o$

ϕ	75	80	85	90	95	100
C(1)-H	1.85	1.95	2.06	2.16	2.25	2.34
Si-H	2.55	2.43	2.31	2.18	2.05	1.93
H(45)-H	1.99	1.92	1.86	1.82	1.80	1.80

The favoured position for the hydrogen atom is

$$\theta = 115 \pm 5^o$$

$$\phi = 85 \pm 5^o$$

and the silicon-hydrogen contact. The manganese-silicon bond appears to be considerably weaker than the rhenium-silicon bond and it is difficult (if not impossible) to separate the contributing factors. Factors worthy of consideration would appear to be:-

(1) enhanced metal-silicon π bonding for rhenium.

(2) weakening of the manganese-silicon bond to offset a very repulsive Si....H interaction.

(3) weakening of the manganese-silicon bond by incipient five coordination i.e. the short Si....H contact ($\sim$1.8 Å) represents a weak bond in the manganese derivative.

Evidence for (1) requires further structural studies and it would appear that a study of the conjugate base species $[(\underline{h}^5\text{-}C_5H_5)M(CO)_2Si(C_6H_5)_3^-]$ (M = Mn, Re) should provide the answer. However, the manganese anionic species is hypothetical and no synthesis is known at this time. Factors (2) and (3) are mutually exclusive and involve the nature of the silicon hydrogen interaction. Unfortunately, all steric arguments that can be used to distinguish these possibilities are based on comparison which would have an unsound statistical basis. For example, the near equivalence of silicon-hydrogen contacts in $(\underline{h}^5\text{-}C_5H_5)Mn(CO)_2HSiCl_2C_6H_5$ and $(\underline{h}^5\text{-}C_5H_5)Mn(CO)_2HSi(C_6H_5)_3$ (references 43 and 20 respectively) would tend to favour the idea of a repulsive silicon-hydrogen contact since the more electronegative substituents of the dichlorophenylsilyl ligand might be expected to promote a silicon-hydrogen bond and hence shorten the silicon-hydrogen contact if it were attractive. However, the hydrogen atoms in these two manganese structures are not located with sufficient precision to allow meaningful discussion.

Chapter Three

The crystal and molecular structure of trans-hydrido-bis (difluoromethylsilyl) (π-cyclopentadienyl) monocarbonyl iron

Introduction

The comparative study of the molecules $(\underline{h}^5\text{-}C_5H_5)M(CO)_2HSi(C_6H_5)_3$ (M = Re, Mn) and $(\underline{h}^5\text{-}C_6H_5)Mn(CO)_2HSiCl_2C_6H_5$ (this work and references 20 and 43 respectively) clearly expresses the problems associated with X-ray diffraction studies when relatively precise information concerning hydrogen atom locations is required. While this type of problem is more properly tackled by neutron diffraction, X-ray diffraction can yield useful data if the study molecule is carefully chosen. The previous chapter indicates two complimentary approaches to the location of the hydride ligand, (1) direct observation and (2) by inference, using arguments based on non-bonded contacts. Arguments based on non-bonded contacts are optimised by increasing the symmetry of the hydride ligand environment and assuming a single well potential. Direct observation should be optimised by choosing a metal in the first transition series. Close silicon-hydrogen contacts are promoted by high coordination of the metal and highly electronegative substituents on the silicon atom. Consideration of all of these factors suggests that the molecules containing the structural fragment $(\underline{h}^5\text{-}C_5H_5)Fe(CO)H(SiXX'X'')_2$ (X, X' and X'' = various substituents) should be particularly suitable. Data on two molecules (XX'X'' = Cl_3[47] and XX'X'' = $(CH_3)_2C_6H_5$[43]) of this class of compounds are available for comparison. In neither of these molecules was the hydrogen located directly. The structure of the bis(di-

fluoromethylsilyl) derivative was undertaken in an attempt to gain further information on this particular series of hydrido metal-silyl compounds.

Experimental

The pale yellow prismatic crystals of $(\underline{h}^5\text{-}C_5H_5)Fe(CO)H(SiF_2CH_3)_2$ as supplied by Dr. W.A.G. Graham and E. Wood were suitable, in terms of size and quality, for an X-ray diffraction study. Since the compound is extremely air-sensitive, individual study crystals were sealed in Lindemann glass capillaries. Well formed crystals showed mmm symmetry with all faces of the forms {100}, {001} and {011} being developed. Preliminary photographic studies using Weissenberg and precession cameras showed the crystals to be orthorhombic and the systematic absences - ($0k\ell$ for $k+\ell$ 2n+1, $h0\ell$ for h = 2n+1) were consistent with two space groups, Pnam (non-standard setting of Pnma (#62)) and $Pna2_1$ (#33). Precise unit cell dimensions were obtained as a = 11.821(2) Å, b = 7.157(2) Å, c = 14.640(2) Å on the manual Picker Four Circle Diffractometer. Twelve intense non-axial reflections were carefully centred in 2θ (no monochromator, CuK_{α_1} radiation, λ = 1.54051 Å) and these measurements were used to refine the rough cell parameters obtained from the photographs mentioned above. The cell parameters were also determined by least squares refinement using, as data the setting angles (χ, ω, ϕ and 2θ) of twelve reflections which were carefully centred on the (then recently acquired) Picker FACS1 diffractometer (MoK_α radiation, λ = 0.71069 Å). The parameters obtained from the FACS programme[48] were as follows:

a = 11.858(12) Å, b = 7.173(4) Å and c = 14.682(18) Å. These parameters average 1.003 times greater than those obtained from the measurements on the manual instrument and probably indicate that the machine centered on the unresolved $K_{\alpha 1}$ peak (λ =0.70926 Å). For four molecules in each unit cell the density was calculated to be 1.64 grms./cm^3. Precise experimental measurement of the density was not possible in view of the reactive nature of the compound, but when a few crystals were introduced into a mixture of organics liquids of approximately this density (within 1%) and introduced into the bulk of this liquid they showed no marked tendency to rise or fall during the minute or so in which no overt change in their appearance occurred.

A fresh crystal of external dimensions 0.1x0.1x0.1 mm was taken and mounted on the Picker FACS 1 diffractometer in an arbitrary orientation and the intensities of 1309 reflections were measured using the coupled $\omega/2\theta$ scanning mode of the Picker diffractometer. A scan width of 3^o in 2θ was chosen and a scanning rate of 1^o/minute employed. Background was measured for 40 seconds on either side of the peak with the detector stationary. Data (limited by $0 < 2\theta < 50^o$) were collected using MoK$_\alpha$ radiation monochromated by an oriented graphite crystal (reflecting plane 002), and a take off angle of 3^o. The scattered X-rays were detected by a scintillation counter used in conjunction with a pulse height analyser tuned to accept 95% of the MoK$_\alpha$ peak. Of the measured intensities 981 were judged to be significant ($I/\sigma I > 3.0$) and were used in the subsequent elucidation and refinement of the structure. No intensities exceeded the linear counting range of the detector and the periodic monitoring of three standard reflections indicated the absence

of decomposition of the study crystal during the data collection procedure. The significant data were reduced to structure amplitudes by correction for Lorentz, polarisation and absorption effects ($\mu = 15\ \mathrm{cm}^{-1}$, transmission factors range from 0.90 to 0.95).

Structure Solution and Refinement

For space group $Pna2_1$ each molecule must occupy a general position whereas for space group Pnam which has eight general positions a molecular symmetry element must be coincident with a crystallographic symmetry element if there are only four molecules in each unit cell. The special positions of space group Pnam correspond to point groups m or $\bar{1}$ of which only the former is possible for $(\underline{h}^5\text{-}C_5H_5)Fe(CO)H(SiF_2CH_3)_2$ in the absence of disorder. The iron and silicon coordinates for the two possibilities are given below.

$Pna2_1$

Fe	x_1,y_1,z_1;	$\bar{x}_1,\bar{y}_1,\frac{1}{2}+z_1$;	$\frac{1}{2}-x_1,\frac{1}{2}+y_1,\frac{1}{2}+z_1$;	$\frac{1}{2}+x_1,\frac{1}{2}-y_1,z_1$
Si(1)	x_2,y_2,z_2;	$\bar{x}_2,\bar{y}_2,\frac{1}{2}+z_2$;	$\frac{1}{2}-x_2,\frac{1}{2}+y_2,\frac{1}{2}+z_2$;	$\frac{1}{2}+x_2,\frac{1}{2}-y_2,z_2$
Si(2)	x_3,y_3,z_3;	$\bar{x}_3,\bar{y}_3,\frac{1}{2}+z_3$;	$\frac{1}{2}-x_3,\frac{1}{2}+y_3,\frac{1}{2}+z_3$;	$\frac{1}{2}+x_3,\frac{1}{2}-y_3,z_3$

Pnam

Fe	$x_1,y_1,\frac{1}{4}$;	$x_1,y_1,\frac{3}{4}$;	$\frac{1}{2}-x_1,\frac{1}{2}+y_1,\frac{3}{4}$;	$\frac{1}{2}+x_1,\frac{1}{2}-y_1,\frac{1}{4}$
Si(1)	x_2,y_2,z_2;	$x_2,y_2,\frac{1}{2}+z_2$;	$\frac{1}{2}-x_2,\frac{1}{2}+y_2,\frac{1}{2}+z_2$;	$\frac{1}{2}+x_2,\frac{1}{2}-y_2,z_2$
Si(2)	$x_2,y_2,\frac{1}{2}-z_2$;	x_2,y_2,z_2;	$\frac{1}{2}-x_2,\frac{1}{2}+y_2,z_2$;	$\frac{1}{2}+x_2,\frac{1}{2}-y_2,\frac{1}{2}-z_2$

[illegible]

For space group $Pna2_1$ the z coordinate of one atom must be assigned to determine the origin in the z direction. The choice of z = 1/4 for the iron atom is convenient and the coordinates for a Pnam model correspond then to the special case for the $Pna2_1$ model when $x_3 = x_2$, $y_3 = y_2$ and $z_3 = 1/2 - z_2$. A three dimensional Patterson[49] map was calculated and the major peaks were identified with vectors for a Pnam solution as shown below.

Peak Position			Peak Height	Vector Assignment
u	v	w		
0	0	0	999	Origin vector
0.28	1/2	1/2	340	Fe-Fe, $1/2+2x_1$, 1/2, 1/2
1/2	0.76	0	340	Fe-Fe, 1/2, $1/2+2y_1$, 0
1/2	1.00	0	175	Si-Si, 1/2, $1/2 \pm 2y_2$, 0
0.40	1/2	1/2	175	Si-Si, $1/2+2x_2$ 1/2, 1/2
0.06	0.12	0.125	100	Fe-Si, x_2-x_1, y_2-y_1 $z_2-1/4$
0	0	1/4	100	Si-Si, 0, 0, $1/2+2z_2$

This assignment gave approximate coordinates for the heavy atoms as

iron x = 0.39, y = 0.13, z = 0.25

silicon x = 0.45, y = 0.25, z = 0.375

The carbon, oxygen and fluorine atoms were located in an electron density map phased by the iron and silicon atoms (R_1 = 26%, R_2 = 35%). The successful identification of a single image in the electron density map tends to support the choice of space group as Pnam, but cannot eliminate a $Pna2_1$ model in which the molecule and its mirror image

superimpose within approximately 0.5 Å for all atoms.

The structure was refined successfully in space group Pnam which provides reasonable evidence for this choice of space group. An outline of the refinement is given in Table (X) below:

Table (X)

An outline of the refinement for $(\underline{h}^5\text{-}C_5H_5)Fe(CO)H(Si(F_2CH_3))_2$

	Model	R1(%)	R2(%)
(1)	Fe, Si isotropic	26	35
(2)	Fe, Si, F, O, C isotropic H's of C_5H_5 at calculated positions	8.6	14.7
(3)	Fe, Si, F, O, C anisotropic H's of C_5H_5 at calculated positions	4.4	7.5
(4)	as (3), but with H's of CH_3 included in calculated structure factors using a hindered rotor model[27].	3.5	5.0
(5)	as (4) with extinction correction[50]	3.1	4.9
(6)	as (5) with addition of H ligand	2.8	4.3
(7)	as (6) except C_5 ring as a hindered rotor[27].	3.3	5.5

Structure factors were calculated using the atomic scattering factors of Cromer and Mann[23] for all atoms except hydrogen where the values of Mason and Robertson[24] were used. The real and imaginary terms for anomalous scattering were included for iron and silicon[25]. The positions

of the hydrogen atoms of the cyclopentadienyl ring were calculated from the following assumptions (1) H atoms were coplanar with the C_5 ring (2) C-H distances of 1.0 Å (3) C-H vector bisecting the appropriate external C-C-C angle. The hydrogens of the methyl group were located in an electron density difference map calculated when R1 = 4.1%. In this difference map a peak consistent with the hydride ligand was also apparent, but was not accepted at this stage since the data appeared to suffer from extinction, although not excessively (maximum correction of the order of 20% of F_{calc}). An extinction correction[50] reduced R1 to 3.1% and the refined value of the extinction parameter was 1.4×10^{-7}.

At this stage of refinement the positive identification of the hydride ligand was attempted. The general procedure was that of Ibers[28]. i.e. using a series of electron density difference maps with varying maximum limits of $\sin\theta/\lambda$ for the contributing data. While the details of this treatment have been criticised[30], the technique does ensure that any observed peak receives appropriate contributions to its electron density from the various shells (ranges of $\sin\theta/\lambda$) of the data set. The results of this study are collected in Table (XI) overleaf. For all maps with a $\sin\theta/\lambda$ limit > 0.25 the largest peak was found at x = 0.50, y = 0.25 and z = 0.20 corresponding to an iron-hydrogen distance of 1.44 Å (the data having been transformed to the standard setting for the centrosymmetric space group Pnma). The x, z and isotropic temperature factors of this hydrogen were refined in two final cycles of least squares refinement. The parameters refined sensibly to give x = 0.497(3), z = 0.191(5) and B = 3.5(8) (y was constrained by symmetry to 0.25). The refined coordinates correspond to iron-hydrogen distances of 1.39(6)Å.

Table (XI)

A table of data extracted from a series of electron density difference maps for the molecule $(\underline{h}^5\text{-}C_5H_5)Fe(CO)H(SiF_2Me)_2$.

Cut off limit in Sinθ/λ	No. of terms in calculations	Observed electron density ρ^E	Error in ρ^E $\sigma(\rho)$ (at y=0.25)	Ratio $E/\sigma(\rho)$	Calculated electron density B = 3.0	Fe-H distance in Angstroms
0.20	51	0.20	0.027	7.4	0.16	1.52
0.25	95	0.31	0.036	8.6	0.25	1.44
0.30	156	0.44	0.042	10.5	0.34	1.44
0.35	241	0.50	0.045	11.1	0.42	1.44
all data	979	0.64	0.053	12.1	not calculated	1.44

The true iron-hydrogen distance is probably between 0.05 and 0.15 Å longer because of bonding effects[51] produce a pronounced deviation from a spherical electron density distribution for hydrogen atoms.

Two cautions are appropriate when discussing the validity of the hydride location. In this case the unit cell is rather small and thus the number of independent terms in the electron density calculations are small and errors in a few observations can produce substantial effects. The data set also suffers from extinction and this increases the concern with this problem. However, the peak assigned to the hydride ligand is located in the same place regardless of the application of the extinction correction and it seems that the known errors in the data are not contributing significantly to this peak.

A final model in which the C_5 ring was treated as a hindered rotor refined to give R1=3.3%, R2=5.5% and was discarded[52] in favour of the previous model.

Results

The observed and calculated structure amplitudes of the preferred model (R1=2.8%) are compared in Table (XII) overleaf. The atomic coordinates thermal parameters and rotor model parameters are collected in Table (XIII) thereafter. Symmetry restrictions prevent some parameters from being refined and these are marked with an asterisk and no standard deviations are reported for them. Following Table (XIII) the intramolecular distances and angles are reported in Tables (XIV) and (XV) respectively.

Table (XII)

Structure Amplitudes (x10)

A comparison of Observed and Calculated Structure Amplitudes (x10) in $(\underline{h}^5\text{-}C_5H_5)Fe(CO)H(SiF_2Me)_2$

Table (XII) contains five pages.

H	K	FOBS	FCAL
L = 0**			
0	2	1451	1483
0	4	173	155
0	6	1007	1024
0	8	1290	1297
0	10	485	519
0	12	195	205
0	14	396	378
0	16	395	383
2	0	1218	1233
2	1	1779	1793
2	2	423	424
2	3	970	951
2	4	1557	1539
2	5	439	438
2	6	273	250
2	7	532	567
2	8	583	568
2	9	895	902
2	10	72	67
2	11	121	120
2	12	180	177
2	13	347	345
2	15	402	390
2	16	166	157
2	17	205	200
4	0	36	31
4	1	386	389
4	2	72	78
4	3	189	146
4	4	1016	1027
4	5	492	508
4	6	295	310
4	7	545	553
4	8	87	94
4	9	498	500
4	10	278	270
4	11	207	216
4	12	512	502
4	13	82	84
4	14	325	324
4	15	287	281
4	16	48	46
6	0	500	484
6	1	238	245
6	2	398	397
6	3	528	571
6	4	253	258
6	5	790	792
6	6	586	606
6	7	60	58
6	8	58	44
6	9	64	74
6	10	40	46
6	11	585	583
6	12	164	161
6	13	379	381
6	14	120	117
6	15	50	46
8	0	195	186
8	1	83	81
8	2	565	584
8	3	526	518
8	4	627	648
8	5	357	360
8	7	43	37
8	8	162	154
8	9	74	72
8	10	347	336
8	11	291	296
8	12	224	218
8	13	127	123
8	14	106	109
10	0	200	204
10	1	423	428
10	2	309	312
10	3	122	119
10	4	367	365
10	5	174	170
10	6	56	45
10	7	208	202
10	9	134	128
10	10	206	205
10	11	112	108
10	12	224	224
12	0	370	371
12	1	147	147
12	2	167	167
12	3	166	169
12	5	214	218
12	6	156	156
12	7	159	156
12	8	242	233
12	9	64	66
L = 1**			
0	1	1472	1473
0	3	732	731
0	5	651	637
0	7	1098	1122
0	9	723	724
0	13	157	154
0	15	282	277
0	17	244	244
1	0	568	527
1	1	641	625
1	2	526	515
1	3	482	463
1	4	801	832
1	5	70	61
1	6	688	704
1	7	62	52
1	8	54	45
1	9	56	61
1	10	95	91
1	11	85	90
1	12	372	372
1	13	101	99
1	14	190	189
1	15	97	93
1	16	90	87
1	17	64	55
2	0	948	928
2	1	665	646
2	2	206	212
2	3	897	920
2	4	649	649
2	5	486	485
2	6	293	298
2	7	404	401
2	8	857	893
2	9	57	8
2	10	316	307
2	11	229	232
2	13	160	163
2	14	267	270
2	15	120	113
2	16	204	210
2	17	65	66
3	0	853	826
3	1	561	554
3	2	559	546
3	3	868	867
3	4	195	175
3	5	434	470
3	6	118	110
3	7	378	392
3	8	337	338
3	9	505	508
3	10	215	205
3	11	333	340
3	12	58	53
3	13	256	262
3	14	57	56
3	15	191	185
3	16	93	85
4	0	50	50
4	1	156	150
4	2	305	315
4	3	625	643
4	4	482	498
4	5	745	741
4	6	118	118
4	7	158	167
4	8	464	494
4	9	196	207
4	10	46	44
4	11	206	194
4	12	325	330
4	13	258	260
4	14	110	105
4	16	175	170
5	0	908	895
5	1	363	376
5	2	434	440
5	4	31	23
5	5	226	238
5	6	235	253
5	7	282	281
5	8	405	404
5	9	111	130
5	10	339	335
5	11	205	208
5	12	216	219
5	13	117	116
5	14	131	128
5	15	56	63
5	16	100	104
6	0	125	120
6	1	192	195
6	2	183	195
6	3	88	78
6	4	869	905
6	5	138	130
6	6	366	367
6	7	320	320
6	8	142	141
6	9	42	41
6	10	233	239
6	11	96	94
6	12	403	389
6	13	72	69
6	15	71	71
7	0	291	277
7	1	430	434
7	2	89	89
7	3	194	199
7	4	216	231
7	5	228	240
7	7	188	186
7	8	58	60
7	9	148	137
7	10	83	79
7	11	157	150
7	12	73	72
7	13	110	112
7	14	81	85
7	15	104	104
8	0	230	225
8	2	217	232
8	3	607	625
8	4	387	401
8	5	346	348
8	6	180	181
8	8	93	88
8	9	218	232
8	10	185	188
8	11	223	218
8	12	240	236
8	13	137	133
9	0	205	193
9	1	66	65
9	2	357	372

H	K	FOBS	FCAL
L = 1**			
9	4	340	347
9	6	155	153
9	8	153	149
9	10	115	115
9	12	106	100
10	0	301	282
10	1	48	43
10	2	99	93
10	3	487	500
10	4	88	90
10	5	256	253
10	6	218	221
10	8	191	186
10	10	100	108
10	11	246	241
10	12	86	84
11	0	156	155
11	1	241	240
11	2	75	79
11	3	131	144
11	5	171	182
11	7	153	153
11	9	111	105
12	0	108	108
12	1	243	236
12	2	167	169
12	4	169	174
12	6	167	171
12	7	215	214
13	0	119	112
13	2	102	104
13	4	93	98
13	6	86	86
L = 2**			
0	0	610	589
0	2	738	711
0	4	175	176
0	6	309	319
0	8	371	366
0	10	165	174
0	12	191	185
0	14	151	154
0	16	121	126
1	0	609	562
1	1	180	186
1	2	108	112
1	3	215	224
1	4	312	328
1	5	854	868
1	6	277	280
1	7	500	505
1	8	391	409
1	9	53	65
1	10	259	250
1	11	333	324
1	12	145	148
1	13	223	218
1	14	110	108
1	15	95	85
1	16	110	109
2	0	626	604
2	1	324	304
2	2	247	228
2	3	158	169
2	4	121	125
2	5	33	47
2	6	336	343
2	7	145	148
2	8	167	180
2	9	301	309
2	10	188	186
2	11	213	219
2	12	174	172
2	14	77	75
2	15	96	95
2	16	125	124
3	0	263	248
3	1	305	294
3	2	967	958
3	3	431	410
3	4	872	892
3	5	153	165
3	6	360	373
3	7	452	455
3	8	494	510
3	9	403	403
3	10	352	350
3	11	137	137
3	12	151	147
3	13	66	66
3	14	196	187
3	15	113	110
3	16	162	157
4	0	549	515
4	1	271	245
4	2	100	90
4	3	242	239
4	4	177	184
4	5	429	438
4	6	108	111
4	7	278	283
4	9	122	132
4	10	61	50
4	11	257	268
4	12	44	47
4	13	132	138
4	15	167	165
4	16	67	63
5	0	726	717
5	1	713	701
5	2	329	317
5	3	438	439
5	4	287	296
5	5	515	540
5	6	556	570
5	7	519	532
5	8	191	192
5	9	344	351
5	10	102	101
5	11	242	247
5	12	148	147
5	13	178	180
5	15	152	145
6	0	157	156
6	1	330	320
6	2	104	95
6	3	205	211
6	4	452	471
6	5	278	288
6	7	357	366
6	8	76	82
6	9	208	204
6	11	133	136
6	13	82	87
6	15	161	157
7	0	449	435
7	1	98	93
7	2	346	358
7	3	427	426
7	4	410	416
7	5	165	162
7	6	497	517
7	7	125	119
7	8	338	351
7	9	141	150
7	10	298	304
7	12	224	217
7	14	147	144
8	0	557	550
8	1	193	182
8	2	113	114
8	3	229	232
8	4	311	317
8	5	147	145
8	6	119	134
8	7	74	70
8	8	230	228
8	9	90	87
8	11	176	172
8	12	99	94
9	0	76	72
9	1	257	250
9	2	51	43
9	3	452	470
9	5	318	326
9	6	119	117
9	7	320	327
9	8	73	73
9	9	355	355
9	11	168	168
9	12	58	66
10	0	340	337
10	1	41	35
10	2	125	127
10	3	62	62
10	4	323	328
10	6	48	33
10	7	46	43
10	8	190	191
10	9	47	44
11	0	346	329
11	2	208	211
11	4	203	204
11	5	47	45
11	6	292	293
11	8	194	191
11	10	139	140
12	0	244	241
12	3	75	63
12	4	142	137
12	5	43	25
12	8	158	162
13	0	111	111
13	1	155	157
13	3	174	170
13	5	157	156
L = 3**			
0	1	102	92
0	3	730	750
0	5	668	681
0	7	317	314
0	9	197	192
0	11	592	585
0	13	197	189
1	0	1181	1130
1	1	317	302
1	2	479	465
1	3	498	493
1	4	54	53
1	5	165	182
1	6	411	421
1	7	213	223
1	8	209	221
1	9	214	212
1	10	225	232
1	11	169	177
1	12	273	284
1	13	125	127
1	14	86	76
1	15	103	106
1	16	86	83
2	0	403	352
2	1	31	36
2	2	442	437
2	3	208	218
2	4	631	644
2	5	111	109
2	6	436	444
2	7	344	345
2	8	120	115
2	9	152	156

H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL
L = 3**				6	8	493	506	12	1	58	55	4	6	280	288
2	10	295	288	6	9	113	119	12	2	99	99	4	7	189	180
2	11	145	148	6	10	109	114	12	3	188	185	4	8	425	439
2	12	278	280	6	11	133	142	12	4	72	75	4	10	311	316
2	13	54	41	6	12	75	64	12	5	191	194	4	11	220	225
2	14	71	65	6	13	121	121	12	6	114	114	4	12	175	176
2	15	137	137	6	14	126	123	13	0	96	95	4	13	142	147
2	16	57	60	7	0	131	125	13	1	54	50	4	14	193	188
3	0	229	215	7	1	401	402	13	2	119	118	5	1	39	30
3	1	442	411	7	2	258	258	**L = 4****				5	2	113	102
3	2	232	226	7	3	265	261	0	0	242	240	5	3	74	69
3	3	701	676	7	4	48	38	0	2	754	693	5	4	204	204
3	4	248	253	7	5	296	312	0	4	1010	1009	5	5	162	169
3	5	202	215	7	6	61	58	0	6	542	542	5	7	59	63
3	6	68	69	7	7	218	234	0	8	122	131	5	8	41	40
3	7	168	160	7	8	180	185	0	10	344	344	5	10	41	37
3	8	64	64	7	9	205	208	0	12	562	571	5	11	89	85
3	9	307	302	7	10	124	129	0	14	176	178	5	12	43	38
3	11	172	180	7	11	219	218	1	0	89	75	5	13	74	72
3	12	95	95	7	13	140	141	1	1	157	144	6	0	271	275
3	13	165	169	8	0	371	363	1	2	261	257	6	1	678	671
3	14	95	92	8	1	403	402	1	3	229	214	6	2	127	122
3	15	169	162	8	3	64	55	1	4	86	83	6	3	40	23
4	0	343	330	8	4	116	112	1	5	112	107	6	4	129	120
4	1	315	311	8	5	74	68	1	6	57	55	6	5	41	42
4	2	176	173	8	6	90	100	1	8	59	48	6	6	72	77
4	3	399	393	8	7	415	432	1	9	63	65	6	7	480	483
4	4	652	660	8	8	291	295	1	10	44	49	6	8	82	87
4	5	306	297	8	9	283	284	2	0	305	308	6	9	295	297
4	7	400	414	8	10	87	97	2	1	505	505	6	10	122	128
4	8	238	248	9	0	226	209	2	2	61	52	6	11	96	96
4	9	147	141	9	1	137	139	2	3	907	902	6	12	105	106
4	10	102	99	9	2	260	261	2	4	574	574	6	13	96	91
4	11	63	68	9	3	53	53	2	5	476	480	7	0	230	229
4	12	217	220	9	4	112	113	2	6	172	179	7	1	93	101
4	15	180	169	9	5	72	71	2	7	185	195	7	2	136	138
5	0	403	388	9	6	49	50	2	8	263	273	7	3	64	66
5	1	235	236	9	7	132	133	2	9	231	226	7	4	43	46
5	2	411	400	9	8	227	228	2	10	56	63	7	5	70	72
5	3	98	104	9	10	161	160	2	11	462	464	7	6	41	51
5	4	461	460	9	11	68	67	2	12	259	265	7	7	114	116
5	5	79	87	10	1	297	292	2	13	271	274	7	8	47	55
5	6	423	440	10	2	76	76	2	15	153	150	7	9	150	159
5	7	106	104	10	3	81	85	3	0	445	434	7	10	47	53
5	8	169	163	10	4	162	159	3	1	140	134	7	11	53	45
5	9	61	61	10	5	47	44	3	2	89	91	8	0	336	335
5	10	161	156	10	6	168	172	3	3	115	115	8	1	352	354
5	11	112	108	10	7	218	222	3	6	98	93	8	2	265	271
5	12	247	254	10	8	89	94	3	7	39	45	8	4	64	67
5	13	43	41	10	9	200	203	3	9	97	99	8	6	184	186
5	14	179	179	10	10	76	79	3	10	52	49	8	7	206	211
6	0	814	796	11	1	199	192	3	12	46	41	8	8	281	283
6	2	425	411	11	4	70	64	4	0	848	838	8	9	204	203
6	3	244	248	11	5	115	116	4	1	197	193	8	10	112	110
6	4	69	71	11	6	64	59	4	2	621	614	9	0	94	91
6	5	294	306	11	7	117	118	4	3	559	547	9	1	86	91
6	6	414	424	11	9	51	55	4	4	98	97	9	2	85	86
6	7	44	39	12	0	234	235	4	5	331	331	9	4	51	56

H	K	FOBS	FCAL
L = 4**			
9	5	90	94
9	6	100	97
10	0	333	336
10	1	191	192
10	2	145	143
10	3	203	213
10	5	198	201
10	6	122	123
10	7	120	121
10	8	256	259
10	9	69	61
11	2	55	59
11	3	51	40
11	4	50	52
12	0	76	64
12	1	170	163
12	2	172	163
12	3	50	47
12	4	244	244
L = 5**			
0	1	88	79
0	3	549	532
0	5	608	588
0	9	117	124
0	11	340	340
0	13	169	171
1	0	523	506
1	1	415	409
1	2	305	289
1	3	215	213
1	4	84	80
1	5	172	176
1	6	70	65
1	7	122	115
1	8	230	226
1	9	148	151
1	10	195	196
1	11	92	97
1	12	81	74
1	13	106	106
1	14	83	92
2	0	65	43
2	1	343	335
2	2	386	372
2	3	212	224
2	4	505	496
2	5	347	355
2	6	236	227
2	7	145	140
2	8	110	119
2	9	138	141
2	10	251	250
2	11	191	193
2	12	192	195
2	13	112	119
3	0	211	212
3	1	320	313
3	2	200	193
3	3	74	83
3	4	281	284
3	5	90	90
3	6	137	135
3	7	184	176
3	8	39	39
3	9	202	200
3	10	75	80
3	11	123	127
3	12	117	117
3	13	100	103
4	0	432	424
4	1	411	417
4	2	39	22
4	3	157	151
4	4	315	301
4	5	135	125
4	6	124	127
4	7	419	438
4	8	145	147
4	9	337	344
4	10	90	90
4	11	148	147
4	12	117	118
4	13	62	54
5	0	124	124
5	2	157	158
5	3	138	132
5	4	182	183
5	5	140	136
5	6	134	135
5	8	123	118
5	9	56	43
5	10	108	113
5	11	91	87
5	12	113	115
6	0	454	448
6	1	117	120
6	2	146	146
6	4	77	74
6	6	299	311
6	8	345	350
6	10	106	104
6	11	42	31
7	0	67	58
7	1	160	165
7	3	222	216
7	5	197	189
7	7	88	90
7	9	62	58
7	10	72	64
7	11	119	119
8	0	325	329
8	1	191	187
8	2	119	123
8	3	125	129
8	5	84	86
8	6	113	120
8	7	207	210
8	8	193	194
8	9	125	128
8	10	45	49
9	0	200	200
9	1	62	56
9	2	206	207
9	4	179	176
9	6	113	113
9	8	79	68
10	0	150	149
10	1	199	194
10	2	140	144
10	4	147	147
10	5	56	60
10	6	142	141
11	0	76	70
11	1	147	144
11	3	141	143
L = 6**			
0	0	205	210
0	2	38	24
0	4	239	251
0	6	96	100
0	8	131	127
0	10	126	119
0	12	170	177
1	0	316	310
1	1	330	328
1	2	260	259
1	3	103	91
1	4	283	283
1	5	136	138
1	6	255	247
1	7	266	269
1	8	228	227
1	9	271	271
1	10	141	145
1	11	97	91
1	12	75	72
2	0	63	67
2	1	78	79
2	2	66	64
2	3	200	200
2	4	191	202
2	5	108	112
2	8	177	183
2	11	97	99
2	12	90	89
3	0	166	145
3	1	55	53
3	2	135	130
3	3	267	264
3	4	149	156
3	5	315	324
3	6	212	211
3	7	133	132
3	8	253	253
3	9	87	91
3	10	153	152
3	11	85	86
4	0	88	94
4	1	134	127
4	2	53	48
4	3	192	197
4	4	48	46
4	5	61	61
4	6	62	56
4	7	178	181
4	8	40	43
4	9	54	54
4	10	50	47
4	11	56	62
5	1	151	152
5	2	48	36
5	3	275	276
5	4	177	171
5	5	319	317
5	6	130	133
5	7	222	225
5	8	63	64
5	9	147	150
5	10	81	87
6	0	44	37
6	1	104	105
6	2	40	48
6	3	160	160
6	5	95	97
6	7	96	96
7	0	224	228
7	1	77	78
7	2	257	256
7	3	67	66
7	4	302	291
7	5	73	79
7	6	247	247
7	7	60	62
7	8	149	153
8	1	49	52
8	3	51	62
8	4	125	122
8	7	75	82
9	0	65	60
9	1	172	169
9	2	51	40
9	3	207	200
9	4	54	50
9	5	176	169
10	0	133	130
L = 7**			
0	1	140	137
0	3	41	29
0	5	99	101
0	7	237	236
0	9	146	136

H	K	FOBS	FCAL
L = 7**			
1	0	272	281
1	1	132	130
1	2	161	158
1	3	113	114
1	4	105	104
1	5	120	125
1	6	150	145
1	7	120	120
1	8	148	151
1	9	136	142
2	0	227	217
2	1	117	115
2	2	94	98
2	4	81	81
2	6	186	194
2	7	146	146
2	8	212	215
2	9	78	70
3	0	57	51
3	1	242	245
3	2	70	64
3	3	176	185
3	4	108	111
3	5	113	118
3	6	51	47
3	7	114	105
3	9	106	107
4	0	237	241
4	1	141	135
4	2	66	66
4	3	183	188
4	4	73	79
4	5	188	194
4	6	99	95
4	7	145	146
4	8	141	143
5	0	222	221
5	1	75	73
5	2	186	192
5	3	59	55
5	4	148	149
5	5	65	71
5	6	108	113
6	1	100	99
6	2	133	126
6	4	276	277
6	6	120	124
7	1	116	112
7	2	65	64
7	3	113	105
7	4	95	87
L = 8**			
0	0	303	304
0	2	160	152
0	6	125	127
1	3	45	34
2	0	191	198
2	1	272	275
2	2	92	90
2	3	117	126
2	5	102	100
3	0	46	35
3	1	52	49
4	0	208	218
4	1	158	161
4	2	223	223

Table (XIII)

Independent atom and group parameters

for $(\underline{h}^5\text{-}C_5H_5)Fe(CO)H(Si(F_2CH_3))_2$

Positional Parameters

Atom	x	y	z
Fe	0.3856(1)	0.2500*	0.1266(1)
C(1)	0.2997(3)	0.2500*	0.3228(5)
C(1)	0.2406(3)	0.2500*	0.4513(4)
Si	0.4529(1)	0.3787(1)	0.2570(1)
F(1)	0.4979(2)	0.3627(1)	0.4654(2)
F(2)	0.5625(2)	0.4190(1)	0.1577(3)
C(2)	0.3547(3)	0.4756(2)	0.2725(5)
C(3)	0.4472(4)	0.2500*	-0.1475(5)
C(4)	0.3788(3)	0.3281(2)	-0.1175(4)
C(5)	0.2701(3)	0.2982(2)	-0.0704(4)
H(1)	0.497(3)	0.2500*	0.191(5)

*constrained by symmetry

Table (XIII)

Thermal Parameters

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe	0.0323	0.0329	0.0318	0.0000	-0.0008	0.0000
C(1)	0.0386	0.0419	0.0469	0.0000	-0.0046	0.0000
O(1)	0.0553	0.0849	0.0511	0.0000	0.0184	0.0000
Si	0.0409	0.0397	0.0497	-0.0068	-0.0031	-0.0056
F(1)	0.0936	0.0743	0.0589	-0.0143	-0.0289	-0.0093
F(2)	0.0486	0.0604	0.1087	-0.0192	0.0136	-0.0033
C(2)	0.0627	0.0446	0.0953	0.0011	0.0010	-0.0203
C(3)	0.0688	0.0877	0.0329	0.0000	0.0107	0.0000
C(4)	0.0888	0.0515	0.0371	-0.0045	-0.0063	0.0121
C(5)	0.0625	0.0651	0.0455	0.0117	-0.0185	0.0049
H(1)	0.0439	isotropic				

Group Parameters for Methyl Hydrogen Atoms

x	y	z	B	Bd	Radius
0.338(2)	0.494(2)	0.274(4)	5.6 (not varied)	0.8(2)	0.91(2)

D	E	F
0.82(3)	1.72(6)	2.25(7)

Table (XIV)

Intramolecular distances in $(\underline{h}^5\text{-}C_5H_5)Fe(CO)H(Si(F_2CH_3))_2$

a) bond lengths between heavy atoms, standard deviations in parenthesis.

Atom 1		Atom 2	Distance
Fe	-	Si	2.249(1)
Fe	-	C(1)	1.733(4)
Fe	-	C(3)	2.092(4)
Fe	-	C(4)	2.089(3)
Fe	-	C(5)	2.086(3)
C(1)	-	O(1)	1.156(4)
Si	-	F(1)	1.591(2)
Si	-	F(2)	1.601(2)
Si	-	C(2)	1.836(3)
C(3)	-	C(4)	1.416(4)
C(4)	-	C(5)	1.398(5)
C(5)	-	$C(5^1)$	1.411(6)

b) from a heavy atom to the hydrogen.

Atom 1		Atom 2	Distance
Fe	-	H(1)	1.49(6) (bonding)
F(1)	-	H(1)	2.57(7)
F(2)	-	H(1)	2.56(7)
Si	-	H(1)	2.06(7)

[illegible]

[illegible]

[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]

[illegible]

[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]

Table (XIV)

c) important non-bonding intramolecular distances between heavy atoms.

Atom 1	Atom 2	Distance
Si	Si'	3.667(2)
Si	C(1)	2.654(3)
F(1)	C(1)	3.042(3)
C(5)	C(2)	3.380(3)
F(1)	F(1)'	3.300(3)

Table (XV)

Table of significant angles between bonds. Angle reported is that subtended about 2_1 by 1 and 3_1 angles in degrees, standard deviations in parenthesis.

Atom 1	Atom 2	Atom 3	Angle
Si	Fe	Si'	113.9(1)
Si	Fe	C(1)	82.6(1)
Si	Fe	H(1)	63
C(1)	Fe	H(1)	109
F(1)	Si	F(2)	105.5(1)
F(1)	Si	C(2)	105.5(1)
F(2)	Si	C(2)	104.8(1)
Fe	C(1)	O(1)	178.6(3)
C(4)	C(3)	C(4')	107.6(4)
C(3)	C(4)	C(5)	108.0(3)
C(4)	C(5)	C(5')	108.2(2)
Fe	Si	F(1)	112.4(1)
Fe	Si	F(2)	114.4(1)
Fe	Si	C(2)	116.6(1)

[illegible]

[illegible]

[illegible]	[illegible]	[illegible]	[illegible]

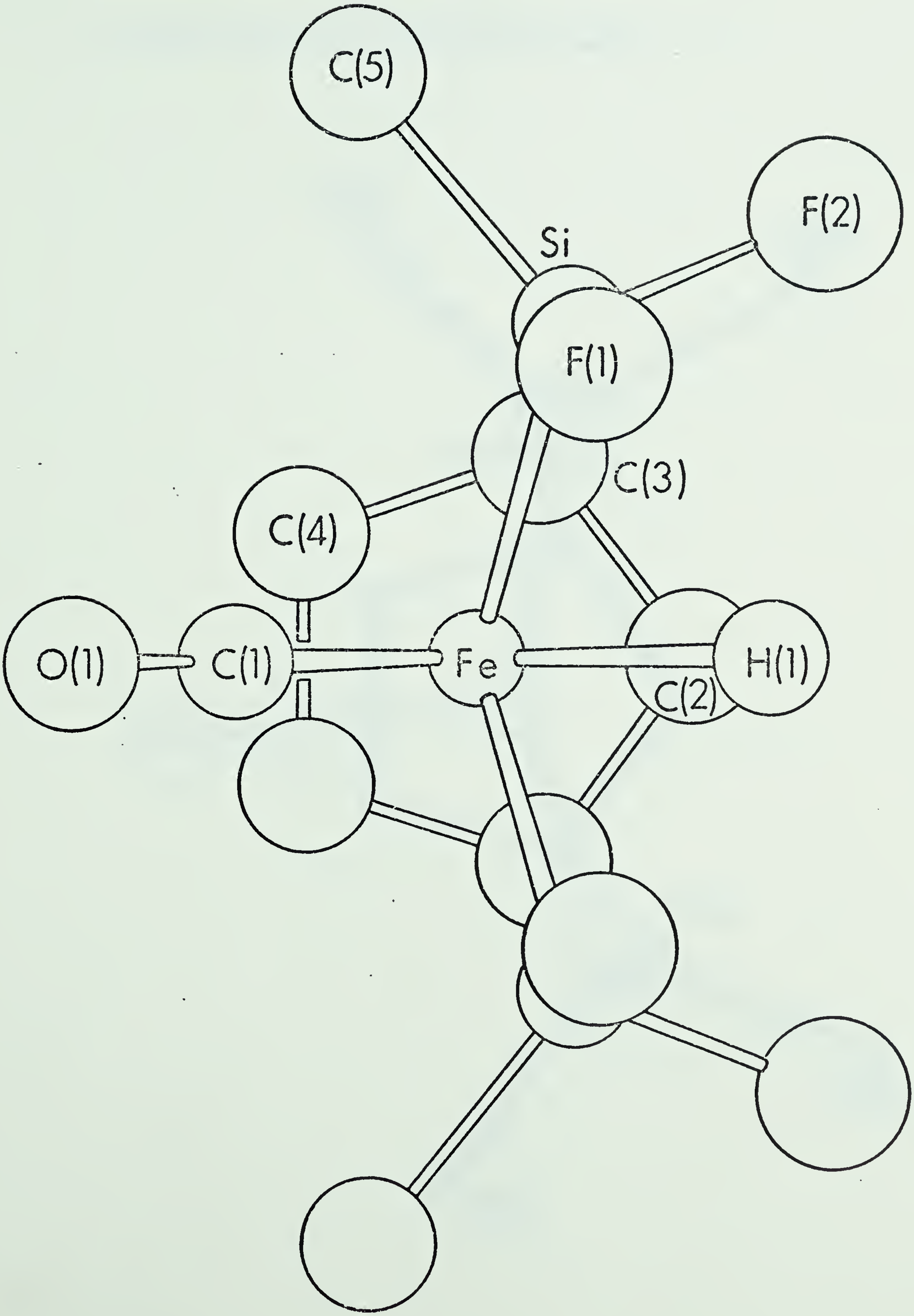
Discussion of the Structure

A view of the molecule as projected onto the plane of the C_5 ring is shown in Figure (VI). The molecular symmetry is as required by the site symmetry. Equivalent views of $(\underline{h}^5\text{-}C_5H_5)Fe(CO)H(SiCl_3)_2$ and $(\underline{h}^5\text{-}C_5H_5)Fe(CO)H(Si(CH_3)_2C_6H_5)_2$ are shown in Figures (VII) and (VIII) respectively. Figures (VI), (VII) and (VIII) follow, in order, on the next three pages. All three structures show the same gross stereochemistry with regard to the orientation of the ligands although minor angular differences are apparent from these diagrams. To a good approximation, the carbonyl group bisects a carbon-carbon bond of the cyclopentadienyl ring in all three structures. The largest deviation from this ligand arrangement is shown by the bis(trichlorosilyl) derivative.

Structural data on the $(\underline{H}^5\text{-}C_5H_5)Fe(CO)Si_2$ fragments of the study molecule and of those discussed above are compared in Table (XVI) and follows Figure (VIII).

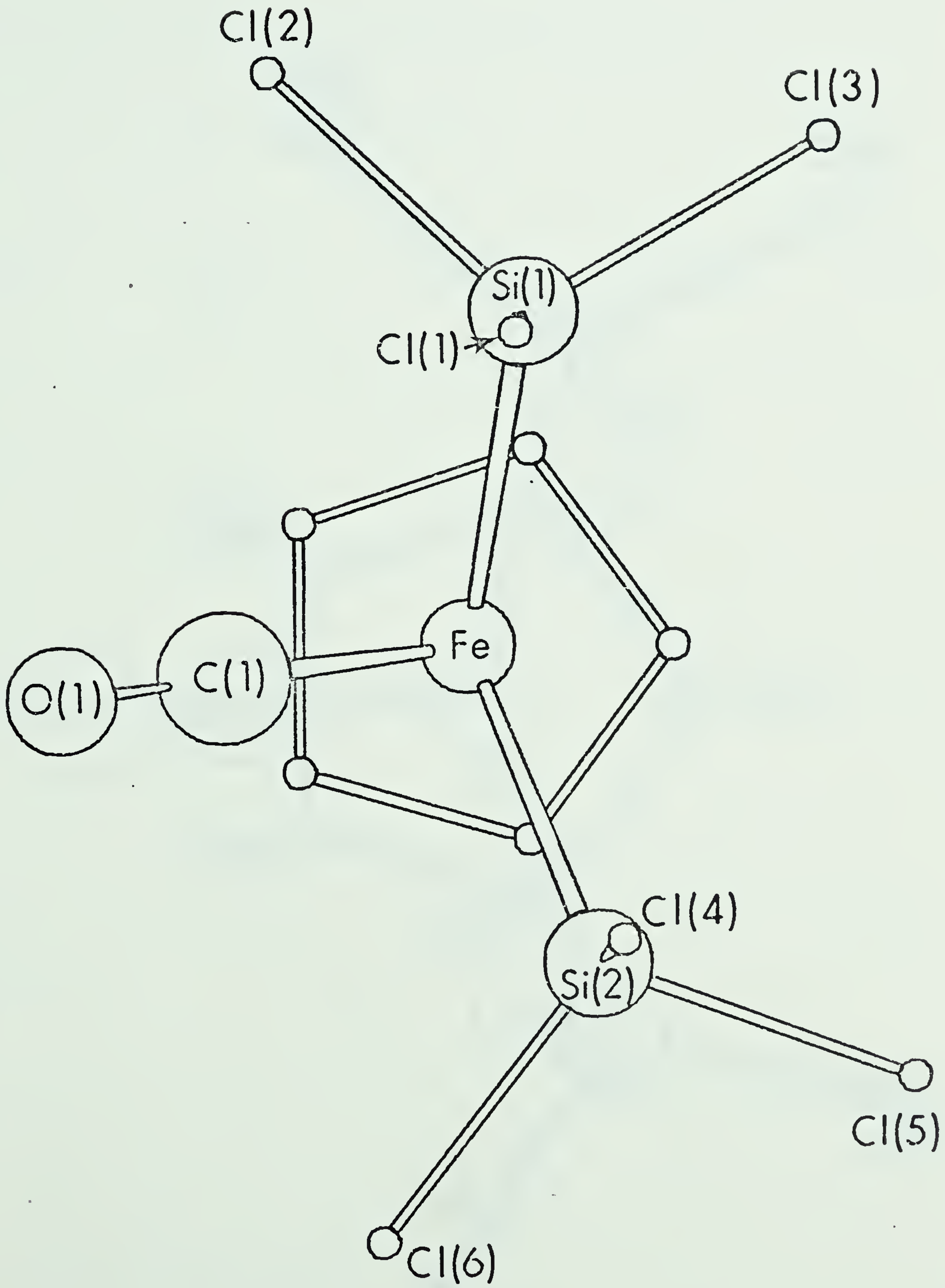
Figure (VI)

A skeletal view of trans-hydride bis(difluoromethylsilyl) (cyclopentadienyl) monocarbonyl iron seen down the vector joining the iron atom to the centre of the cyclopentadienyl group.


C(5)
F(2)
Si
F(1)
C(3)
C(4)
O(1)
C(1)
Fe
H(1)
C(2)

Figure(VII)

A similar view of the trichlorosilyl analog



Figure(VIII)

A similar view of the dimethylphenylsilyl analog

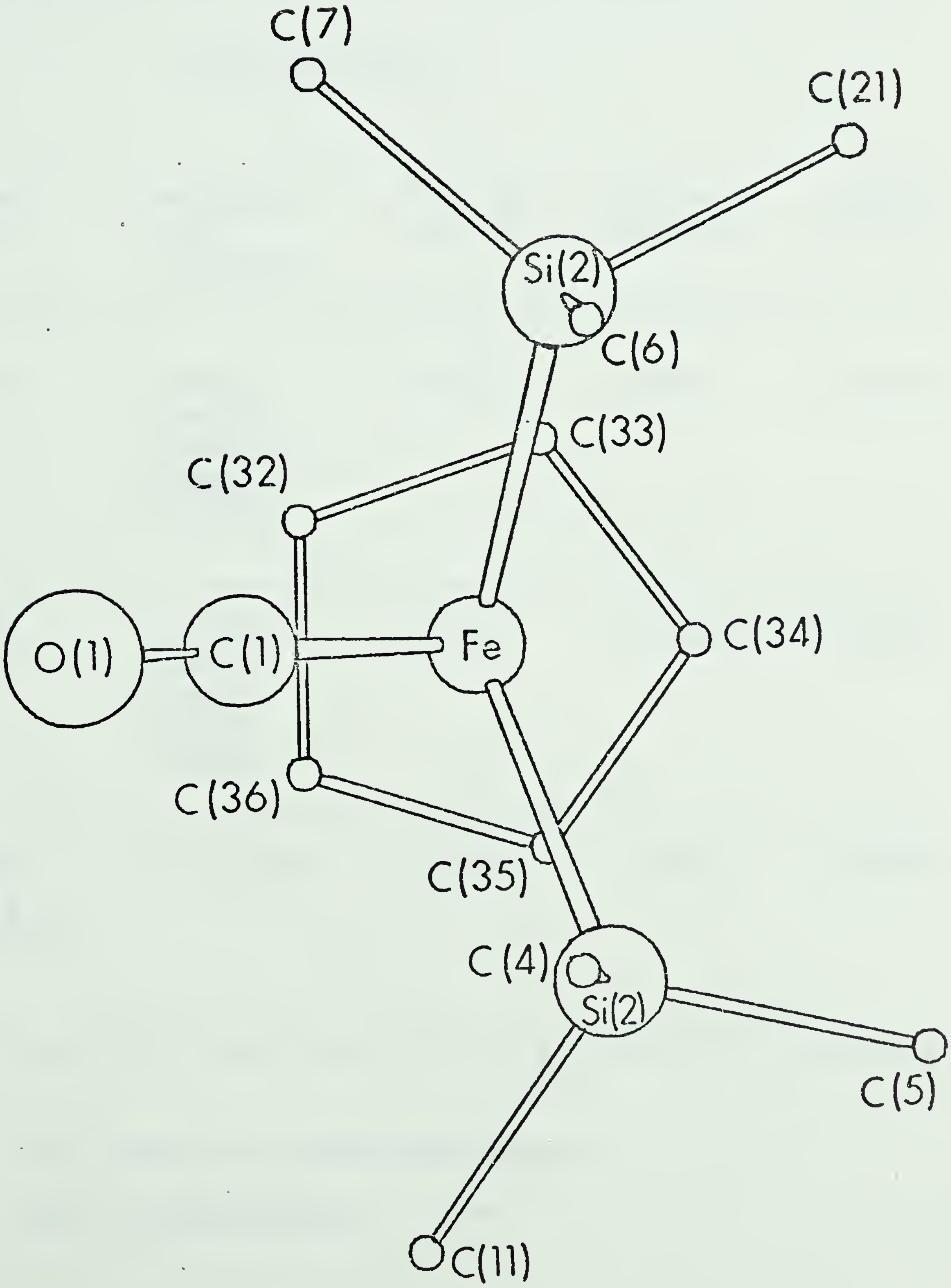


Table (XVI)

A comparison of the reported structures of the form

$(\pi\text{-cpd})HFeCO(SiR_3)_2$

Molecule and Reference No.	Individual Fe-C Distances	Fe - cp Distance	Fe-C(CO) Distance	Fe-Si Distance
$(\pi\text{-cpd})HFeCO$ $(SiF_2Me)_2$	2.086(3), 2.089(3), 2.089(3), 2.092(4), 2.092(4)	1.72(1)	1.73(1)	2.249(1)
$(\pi\text{-cpd})HFeCO$ $(SiH_3)_2$ Ibers[20]	2.10(1), 2.10(1), 2.09(1), 2.09(1), 2.08(1)	1.72(1)	1.76(1)	2.252(3)
$(\pi\text{-cpd})HFeCO$ $(Si(CH_3)_2C_6H_5)_2$ Simpson[43]	all 2.10(1)	1.72(2)	1.71(1)	2.336(3)

cp = centre of cyclopentadiene ring

cpd = cyclopentadiene

The iron to carbon (cyclopentadienyl) distances exhibit remarkable consistency within each molecule and are independent of the silyl substituents. This provides more evidence that highly electronegative substituents on silicon do not cause a contraction of the metal d orbitals in carbonyl derivatives. The equality of the iron-silicon bonds in the difluoromethylsilyl and trichlorosilyl derivatives at 2.25 Å would suggest an equality in the electron withdrawing ability of these groups. Table (XVII) contains values for the sums of the electronegativities of the silicon substituents (excluding the metal) for SiF_2CH_3 and SiF_3 for three different scales of electronegativity.

Table (XVII)

Electronegativity sums for silicon substitutents (excluding the metal).

SiF_2CH_3	$SiCl_3$	SiF_3	Reference
10.70	8.49	12.30	53
10.51	9.48	11.94	54
10.45	9.00	11.73	55

For all three scales the ligand ordering would be $SiF_3 > SiF_2CH_3 > SiCl_3$.

The structural studies of $Co(CO)_4SiF_3$ and $Co(CO)_4SiCl_3$ show[13] a small difference in cobalt-silicon bond lengths of only 0.02 Å. Since SiF_2CH_3 is judged to be intermediate between SiF_3 and $SiCl_3$ one might expect a difference of approximately 0.01 Å in iron silicon bond lengths in the trichlorosilyl and difluoromethylsilyl derivatives. Given the errors associated with the iron silicon bond lengths a difference of this magnitude could not be detected with reasonable certainty. The considerably longer iron-silicon bond length observed in $(\underline{h}^5\text{-}C_5H_5)Fe(Co)H(Si(CH_3)_2C_6H_5)_2$ is in accord with the relatively low electronegativity of the substituent carbon atoms. The iron carbonyl linkages in all the structures fall in the range 1.71 Å to 1.76 Å with errors that preclude a statistically sound comparison.

The silicon-carbon (1.836(3) Å) and silicon fluorine (1.591(2), 1.601(2) Å distances of the difluoromethylsilyl substituents are essentially identical with those observed in difluoromethyl silane[56] (Si-C = 1.833(2) Å, Si-F = 1.583(2) Å). The hydride ligand is 2.1 Å from each of the two silicon atoms.

Any discussion of geometric parameters associated with hydrogen atoms bound directly to transition metals must be considered somewhat speculative whenever the experimental method is X-ray diffraction. Even a perfect X-ray diffraction study would give metal-hydrogen distances that would be systematically short due to the perturbation of electron density by bond formation[51]. If the magnitude of this shortening is estimated to be 0.1 Å the iron hydrogen distance can be corrected to 1.5 Å which is reasonable when compared with the value of 1.60 Å observed for a manganese-hydrogen bond length in the neutron diffraction

study of $Mn(CO)_5H$[57] and considering the normal trend in covalent radii i.e. Fe < Mn.

An error in the iron-hydrogen vector length makes remarkably little difference to the silicon-hydrogen contact provided the angular parameters are constant. In the case of $(\underline{h}^5\text{-}C_5H_5)Fe(CO)H(SiF_2CH_3)_2$ changing the iron hydrogen distance from 1.4 to 1.6 Å while maintaining Si-Fe-H angle at 63° produces relatively small change in silicon hydrogen contacts from 2.04 to 2.09 Å. Provided that the hydrogen occupies a single minimum potential the molecular mirror plane places a constraint on the direction of the iron-hydrogen vector and only one variable angular parameter is required to define the vector orientation. The convenient angular parameter is that formed between the iron to centroid (of the cyclopentadienyl ring) vector and the iron-hydrogen vector corresponding to the angle θ in the equivalent treatment of $C_5H_5Re(CO)_2HSi(C_6H_5)_3$ in the previous chapter. The consequences of allowing this angle to vary by $\pm 5^{\circ}$ from the observed θ value of 122.5° are shown below.

	Si----H	F(1)----H	F(2)----H
117.5	2.11	2.65	2.57
122.5	2.06	2.56	2.59
127.5	2.02	2.46	2.62

(Fe - H = 1.5 Å assumed)

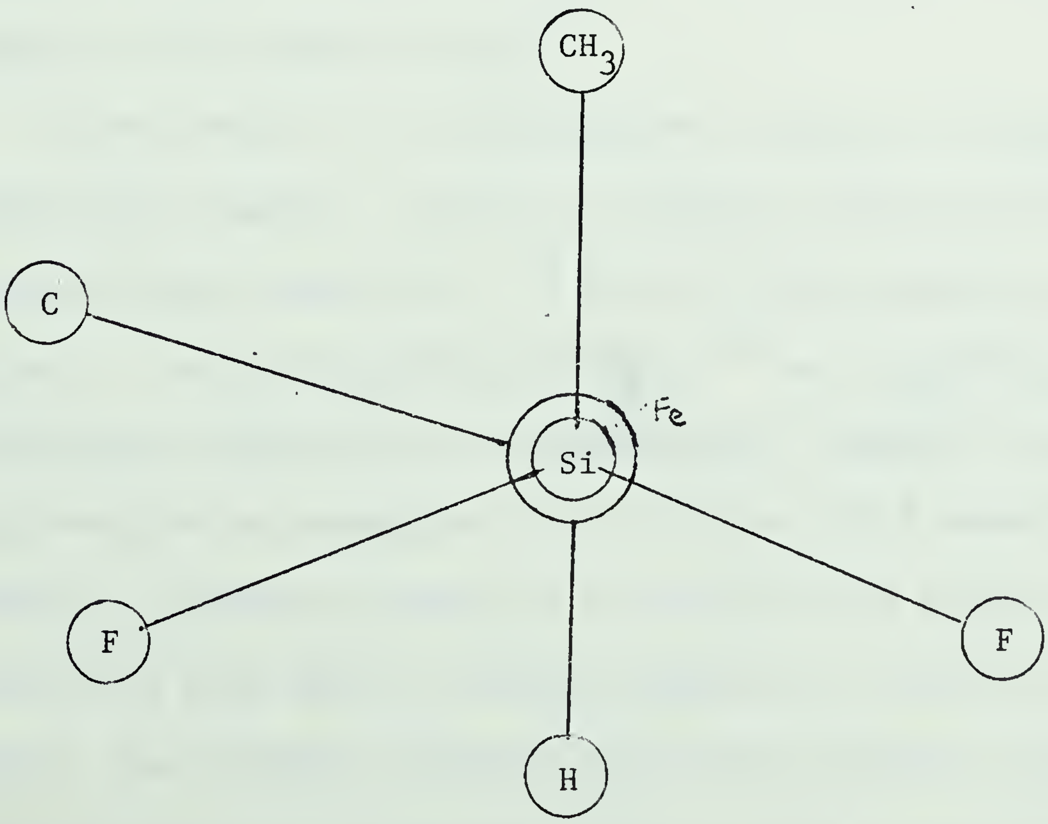
This data shows that the Si - H distance is relatively insensitive to the changes in θ but the fluorine-hydrogen contacts become markedly different. The fluorine-hydrogen contacts are relatively close to van der Waals contacts and in any non-bonded repulsion calculation

using spherical potentials these contacts would constitute little to the overall energy of the system. However, in any sophisticated treatment, that attempted a correction for the perturbation of the spherical electron density due to bonding effects, an equality of the hydrogen-fluorine contacts would assume greater significance since it would correspond to moving the hydrogen atom from a position near an electron deficient antibonding region of a silicon atom towards an electron rich bonding region where repulsion would be expected to be greater for a given internuclear separation.

The conformation of one SiF_2C group relative to the structural fragment FeH(CO) as viewed down the iron-silicon bond is shown in Figure (IX).

Figure (IX)

A demonstration of the staggered conformation adopted by certain atoms in $(\underline{h}^5\text{-}C_5H_5)Fe(CO)H(Si(F_2CH_3)_2$,



It is clear from this diagram that both the carbonyl and hydride ligands adopt a staggered conformation with respect to the substituents of the silyl ligand.

The molecules $(\underline{h}^5\text{-}C_5H_5)Fe(CO)H(SiCl_3)_2$ and $(\underline{h}^5\text{-}C_5H_5)Fe(CO)H(Si(CH_3)_2C_6H_5)_2$ do not have mirror symmetry in the crystalline state and a comparison of the Figures (VI), (VII) and (VIII) shows that some variation in the orientation of the silyl groups is possible due to minor perturbations such as intermolecular forces. Nevertheless the differences in rotations about the iron-silicon bonds are small and it seems reasonable to conclude that in all three molecules the hydrogens will be approximately equidistant from two of the substituents on each silyl ligand. This conformational feature is consistently observed in all transition metal complexes where a hydride ligand forms a close contact with a cis silyl ligand. Only in $Fe(CO)_4HSi(C_6H_5)_3$ where the iron-silicon contact is 2.8 Å does the silyl group fail to adopt a special orientation with respect to the hydride ligand[43].

In the series of iron derivatives containing the $C_5H_5Fe(CO)HSi_2$ structural fragment, the silicon hydrogen contacts are estimated to be greater than or equal to 2.1 Å and have been treated as repulsive in nature. For the $C_5H_5Mn(CO)_2HSi(C_6H_5)$ [20] and $C_5H_5Mn(CO)_2HSiCl_2C_6H_5$ [43] derivatives containing the $C_5H_5Mn(CO)_2HSi$ fragments the silicon-hydrogen cis contacts are estimated to be 1.8 Å and 2.0 Å respectively. The hydrogen apparently prefers to be closer to the silicon atom than to the carbon atom which is totally unexpected in view of the relative atom sizes. The original deduction that this indicated a bonding interaction between silicon and hydrogen atoms (i.e. the onset of the penta coordi-

nation) should be reconsidered.

A terminal carbonyl group with its cylindrical electron density would be expected to be uniformly 'hard' with respect to non-bonded contacts with <u>cis</u> ligands. A silicon atom in an sp^3 hydridised state and with an appropriate orientation appears to be capable of contacts which are of the same magnitude as contacts with carbon atoms of carbonyl groups. The near equality of silicon-carbon and carbon-carbon contacts (at 2.55 and 2.51 Å respectively) in $W_2(CO)_8H_2(Si(C_2H_5)_2)_2$ [43] provides good evidence for this. Thus, the relative ordering of silicon-hydrogen and carbon-hydrogen contacts in the manganese compounds may not be significant. Resolution of this problem requires precise hydrogen co-ordinates and neutron diffraction studies are clearly required.

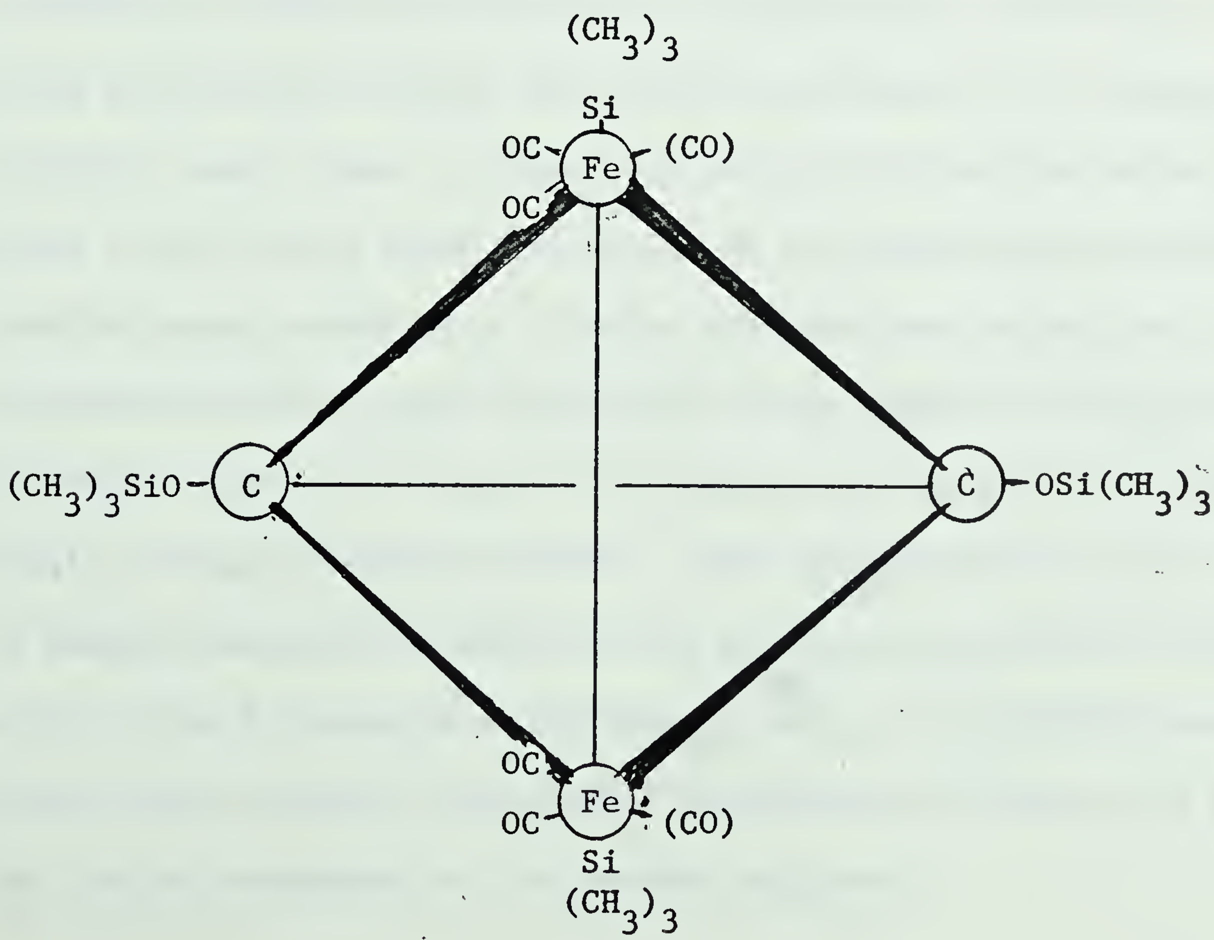
Chapter Four

Introduction

An unusual product assigned the dimeric formula $((Me_3Si)_2Fe(CO)_4)_2$ resulted from the reaction of Me_3SiI with $Na_2Fe(CO)_4$ in tetrahydrofuran[58,59]. An interesting structure based on an Fe_2C_2 tetrahedron was proposed, and it seemed that the reaction provided a further example of the sometimes unexpected course of reactions between organosilicon halides and metal carbonyl anions. The structure,proposed by MacDiarmid,contained the core shown below in Figure(X).

Figure (X)

The core of the molecule as proposed by MacDiarmid.



An anomalous feature of the data reported was the appearance in the mass spectra of the ions $((Me_3Si)_4Fe_2(CO)_9)^+$ and $((Me_3Si)_4Fe(CO)_{10})^+$ in greater abundance than those of the presumed molecular ion. The previous assignment of these kinds of peak as (P+CO) and (P+2CO) seemed improbable[60]. In an attempt to vindicate the useful principle that the peak of largest m/e in the mass spectrum of a metal carbonyl derivative normally gives the minimum number of carbonyl groups present[61], the crystal structure of the compound was undertaken.

Experimental

Yellow prismatic air-sensitive crystals of the compound were kindly supplied by Drs. R.P. Stewart, Jr. and W.A.G. Graham of the University of Alberta. The crystals were grown in a manner suitable for diffraction work by sublimation in vacuo. A preliminary diffraction study using photographic methods indicated Laue symmetry $\bar{1}$ and suggested a triclinic space group. A fresh crystal of external dimensions 0.03 x 0.025 x 0.05 cm was taken and sealed in a Lindemann glass capilliary under an argon atmosphere. This crystal was then mounted at a random orientation upon a Picker Four Circle fully automated (FACS) diffractometer. Three low 2θ axial reflections were located and used to obtain a rough orientation matrix. This matrix was then used to locate 12 intense non-axial reflections and these were carefully centered in ω, 2θ, χ and ϕ (Graphite Monochromator, MoK_α, λ =0.71069 Å) and these values used to obtain precise cell parameters by least square procedure. The lattice parameters of the reduced cell are:

$a = 11.535(12)$

$b = 12.288(12)$

$c = 12.543(12)$

$\alpha = 72.01(6)$

$\beta = 87.31(8)$

$\gamma = 88.08(8)$

giving a calculated density of 1.34 g/cc on the basis of two formula units of $((Me_3Si)_3Fe(CO)_5)_2$ per unit cell. A large, badly formed crystal was found and introduced into potassium iodide solution made up to close to this density (1.32 g/cc). The crystal decomposed in less than a minute but was observed to behave as if it were of similar density to the ambient liquid. The reflections were punched onto paper tape and these were interpreted and punched onto cards with the aid of a programme written and kindly supplied by G. Williams of the Biochemistry Department of the University of Alberta. A 2θ scan method through 2^o with a scan rate of 2^o per minute was employed for the intensity measurement (Graphite monochromator, MoK_α, $\lambda = 0.71069$ Å). Background was counted for ten seconds on either side of the peak with the stationary counter. The reflection data were then transformed to MIXG2 format and reduced to $|F|$ and σF in the usual manner[22]. Of the 3108 intensities measured 1486 were greater than $3\sigma I$ and were used in subsequent calculation. Crystal decomposition was monitored by measuring the intensity of three reflections every hour. Absorption corrections were applied with the aid of the programme GONO9.

Solution and Refinement of the Structure

The space group $P\bar{1}$ was indicated by the statistical distribution of $|E|$'s and was assumed for subsequent calculations. A Patterson map was computed and the positions of the two iron atoms found. The expected vectors and their weights are derived below.

2 independent iron atoms at $x_1y_1z_1$, $x_2y_2z_2$.

$$x_1 - x_2 = \Delta x \qquad x_1 + x_2 = \Sigma x$$

	$x_1y_1z_1$	$x_2y_2z_2$	$\bar{x}_1\bar{y}_1\bar{z}_1$	$\bar{x}_2\bar{y}_2\bar{z}_2$
$x_1y_1z_1$	0 0 0	$\bar{\Delta}x\bar{\Delta}y\bar{\Delta}z$	$\overline{2x}_1\overline{2y}_1\overline{2z}_1$	$\bar{\Sigma}x\bar{\Sigma}y\bar{\Sigma}z$
$x_2y_2z_2$	$\Delta x\Delta y\Delta z$	0 0 0	$\bar{\Sigma}\bar{x}\Sigma\bar{y}\Sigma\bar{z}$	$\overline{2x}_2\overline{2y}_2\overline{2z}_2$
$\bar{x}_1\bar{y}_1\bar{z}_1$	$2x_12y_12z_1$	$\Sigma x\Sigma y\Sigma z$	0 0 0	$\Delta x\Delta y\Delta z$
$\bar{x}_2\bar{y}_2\bar{z}_2$	$\Sigma x\Sigma y\Sigma z$	$2x_22y_22z_2$	$\bar{\Delta}x\bar{\Delta}y\bar{\Delta}z$	0 0 0

Weight	Vector
2	$\Delta x\Delta y\Delta z$
2	$\Sigma x\Sigma y\Sigma z$
1	$2x_12y_12z_1$
1	$2x_22y_22z_2$

[illegible]

Peaks of appropriate size were found at

0.08	0.18	0.86
0.22	0.56	0.48
0.30	0.74	0.34
0.14	0.38	0.62

leading to an assignment of iron positions as;

Fe(1)	0.15	0.37	0.17
Fe(2)	0.07	0.19	0.31

The four silicon atoms were located in an electron density difference map calculated from structure factors phased by the iron atoms (R = 42%). None of the silicon atoms were located within bonding distance of the iron atoms, a feature clearly at variance with the proposed structre. A second electron density difference map, which was phased on the model of two iron atoms and four silicon atoms (R = 35%) contained 32 peaks which appeared suitable for assignment as carbon or oxygen atoms. Twelve of the peaks were readily assigned to terminal carbonyl groups and another twelve peaks seemed consistent with methyl substituents of the silicon atoms. For the remaining eight peaks a definite assignment as carbon or oxygen atoms was not clear. These uncertain peaks were assigned as carbon atoms for the initial stages of refinement of the structure. During the least squares refinement of the model parameters the isotropic temperature factors of four of the uncertain atoms refined to very low values ($\sim$1.5) compared with typical values of 3.5 for the four atoms in the central core of the molecule. This is the effect

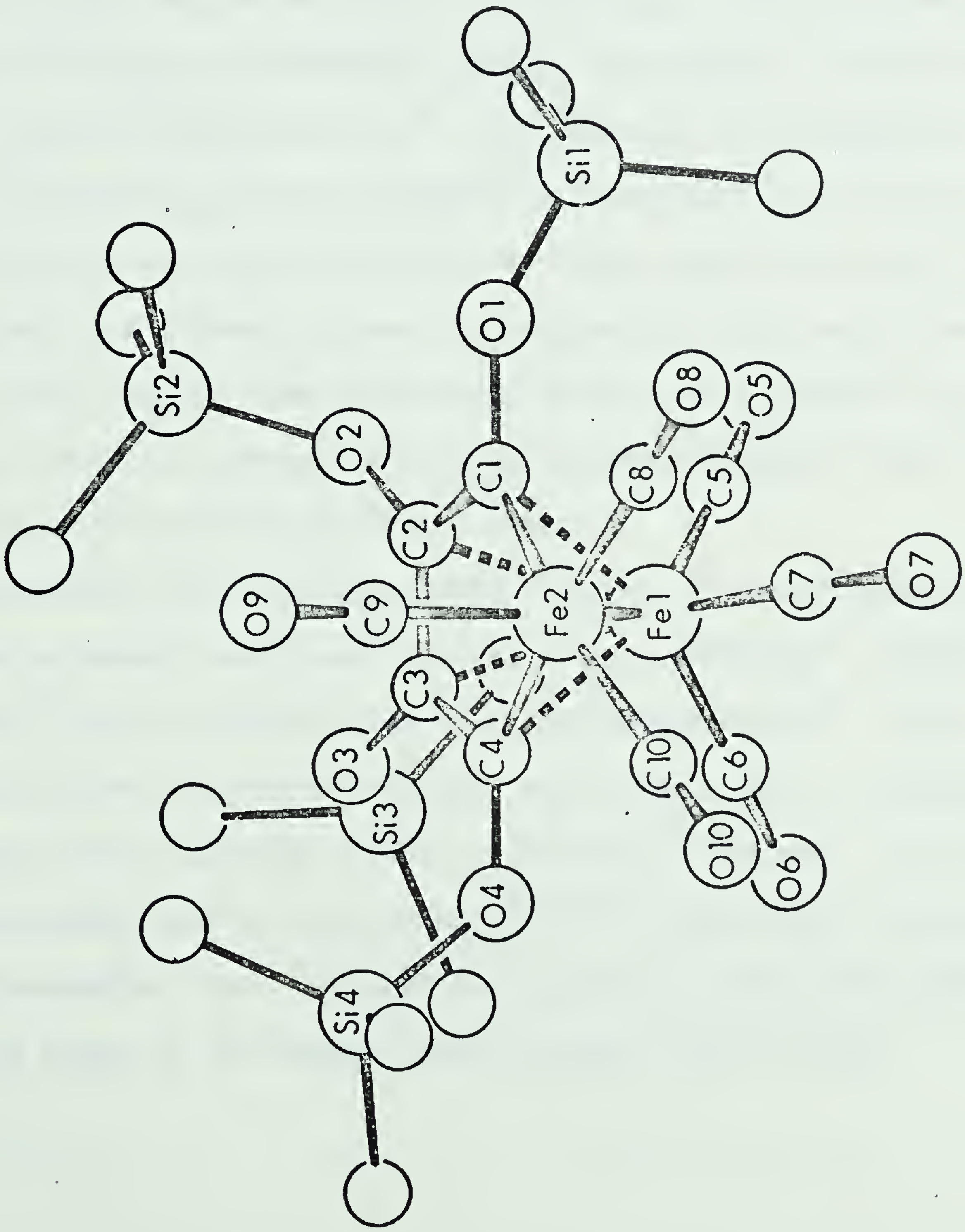
expected when an atom is assigned a scattering factor with too few electrons. Reassignment of these four peaks as oxygen atoms completed the identification of the material. Neutral atomic scattering factors[23] were used for all atoms and the real and imaginary components for anomalous scattering were included for the iron and silicon atoms[25]. An electron density difference map computed at the end of isotropic refinement (R = 12%) indicated substantial anisotropy of vibrations and failed to detect the hydrogen atoms of the methyl groups. The small data set precludes extensive use of anisotropic thermal parameters. Only the heavy atoms (iron and silicon) and the four oxygen atoms of the siloxy groups were allowed anisotropic thermal parameters in the final stages of refinement. Contributions of the methyl group hydrogens to the structure factors were calculated using the hindered rotor model[27] in a free rotor approximation (Bd set at 0.05), but no refinement of the rotor parameters was attempted. The refinement of this model converged at R = 8.5%. The rather high R value reflects difficulty with crystal decomposition and inadequacy of the thermal models of the peripheral atoms. Nevertheless the results are sufficient to confirm the correct chemical composition as given by the mass spectrum, and to establish the structure of the molecule.

Results and Discussion

The molecular structure, shown in Figure (XI) overleaf, confirms the reformulation as $Fe_2Si_4C_{22}H_{36}O_{10}$. The molecule contains a substituted butadiene fragment bonded to one $Fe(CO)_3$ group with two sigma bonds to

Figure(XI)

A perspective view of the bis(trimethylsilyl) iron pentacarbonyl dimer.

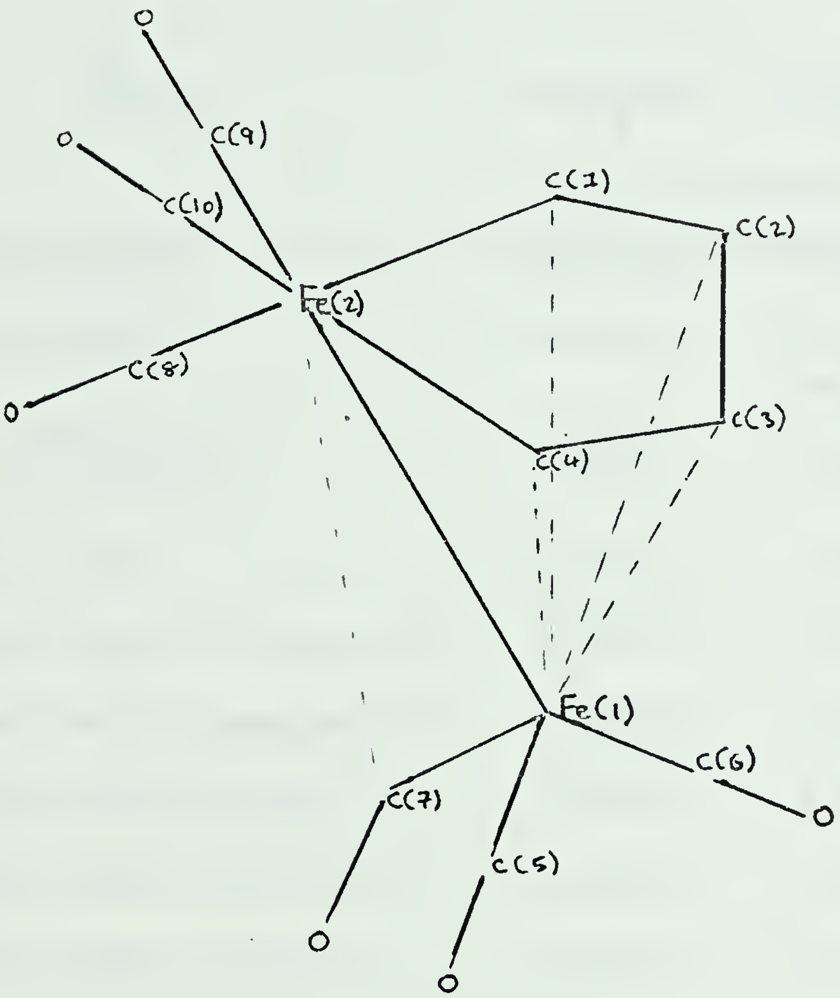


form an iron-containing heterocyclic diene. The five membered ring is π bonded to a second $Fe(CO)_3$ group and an iron-iron bond (2.49 Å) completes the linkage between the two non-equivalent $Fe(CO)_3$ groups. Each carbon atom of the FeC_4 ring has a trimethylsiloxy substituent and appears to have been derived from a carbonyl group. That all four trimethyl silyl groups are attached to oxygen is unexpected, in that only two are cleaved by anhydrous HCl[59]. The compound is an analogue of $(CO)_6Fe_2C_4(OH)_2(CH_3)_2$ whose synthesis[62] and structure[63] have been reported, but in this case only two of the carbon atoms of the FeC_4 ring are derived from carbonyl groups. The mechanism of the overall reaction is not clear, but poses the interesting question as to whether the silicon is directly attached by carbonyl oxygen or migrates there after initial formation of an iron silicon bond.

The geometry of the $Fe(CO)_3C_4Fe(CO)_3$ portion of the molecule shows excellent agreement with those reported by Hoch and Mills[63], Jeffreys and Willis[64] and by Van Meersche, Piret and Meunier-Piret[65]. These three structures are treated in detail after Figure (XI) in conjunction with Figure (XII) and Table (XVIII) in the body of the text. The atom numbering scheme used by these authors[63,64,65] shows little consistency and in consequence their distances are reported in terms of the atom numbering scheme of the fragment shown overleaf (Figure (XII)).

Figure (XII)

A schematic fragment of Reppe-type compounds.



Compound A[63]	$(HOC{:}CMe{\cdot}CMe{:}COM)Fe_2(CO)_6$
Compound B[64]	[1,1,1-tricarbonyl-2,3-dimethoxy-5-(diphenyl-methyl) ferracyclopentadiene] iron tricarbonyl
Compound C[65]	$(C_6H_5{\cdot}C{:}CH{\cdot}C_6H_4)Fe_2(CO)_6$
Compound D	This work i.e. $[Me_3SiOC]_4Fe_2(CO)_6$

The bonds lengths reported are reproduced in the following Table (XVIII).

Table (XVIII)

A table comparing dimensions in various Reppe-type compounds.

Bond	Compound A	Compound B	Compound C	Compound D
		(standard deviations not reported)		
Fe(1)-Fe(2)	2.493(2)	2.54	2.520(3)	2.494(4)
Fe(2)-C(7)	2.48(1)	not reported	2.47(1)	2.52(3)
Av. (C(1)-C(2) (C(3)-C(4)	1.42(1)	1.40	1.42(2)	1.40(2)
C(2)-C(3)	1.43(1)	1.39	1.39(2)	1.39(2)
Av. Fe(2)-C(terminal CO)	1.78(1)	1.76	1.76(1)	1.82(4)
Av. Fe(1)-C(terminal CO)	1.76(1)	1.73	1.75(1)	1.72(3)
Av. Fe(2)-C(1),C(4)	1.94(1)	1.93	1.97(1)	1.92(4)
Av. Fe(1)-C(1),C(4)	2.12(1)	2.14	2.16(1)	2.13(3)
Av. Fe(1)-C(2),C(3)	2.15(1)	2.14	2.16(1)	2.19(3)
Average Fe(1)-C(7)-O(7) angle	168^{o}	172^{o}	165^{o}	166^{o}

In the simplest bonding description of this structure Fe(1), which achieves an inert gas configuration by the donation of six electrons from its carbonyl groups and four electrons from the ferracyclopentadiene fragment, acts as a donor to Fe(2), i.e. both electrons of the iron-iron bond are supplied by Fe(1). This description while convenient for electron counting, is clearly oversimplified, since the large deviation from 180^{o} of the angle Fe-C(7)-O(7) in all four structures indicates some participation by C(7) in the bridge. The iron-iron bond length at 2.494(4) Å appears typical for this class of compounds, but is relatively short in terms of the total range of distances 2.48 Å to 3.00 Å which have been treated as indicative of iron-iron bonds[66-69]. The short metal-metal bond is promoted by bridging (atoms C(1) and C(4)) and the staggered arrangement of the bond Fe(1)-C(7) with respect to the bonds Fe(2)-C(8) and Fe(2)-C(10).

Since the light atoms in this structure are determined with low precision discussion of bond lengths involving light atoms will be restricted to trends that are evident in all four compounds. The geometry of the butadiene fragment of the ferracyclopentadiene ring is similar to that normally observed for butadiene iron tetracarbonyl complexes[70,71]. The deviations of this geometry from the ground state geometry of butadiene has been discussed by Mason and Churchill in terms of a significant contribution from the first excited state for butadiene[72]. While the pattern of carbon-carbon bonds in ferracyclopentadiene iron tricarbonyl derivatives is similar to that found in normal butadiene iron tricarbonyl fragments a marked difference is observed in the pattern of iron-carbon distances. In typical butadiene-iron tricarbonyl systems, the iron atom

is closer to the atoms C(2) and C(3) than to the atoms C(1) and C(4) by approximately 0.1 Å [70,72-79] whereas in the metal-metal bonded ferracyclopentadienyl systems the iron-carbon distances are observed to be equal or the bonds Fe-C(1) and Fe-C(4) are shorter than the bonds Fe-C(2) and Fe-C(3).

The siloxy sidechains exhibit a marked variation in geometry. These substituent groups are arranged in a manner that minimise intramolecular repulsions, with each C_{ring}-O-Si plane (deviations 3^{o}, 3^{o}, 17^{o} and 3^{o}) and with silicon atoms alternately up and down with respect to the FeC_4 plane. The large range of C_{ring}-O-Si angles (123^{o}-147^{o}) as a result of these rather weak forces is in accord with the concept of a "soft" angle at oxygen as suggested by spectroscopic[80] and structural[81] studies. This result strongly suggests that solid state structures of siloxy derivatives are of little utility in attempts to correlate the angles at oxygen with such effects as $d\pi$-$p\pi$ bonding. Such attempts should be based on gas[82] or liquid phase studies. The silicon-carbon distances average 1.86 Å which is close to the value 1.88 Å which is observed in alkyl silanes[83].

A list of heavy atom parameters is given in Table (XIX) overleaf. Hydrogen atom positions, derived from hindered rotors, structure amplitudes, bond lengths, bond angles and the results of least squares calculations on the FeC_4 plane and the four Si-O-C planes appear in Tables (XX)-(XXIV).

Table (XIX)

Atomic Parameters for $((CH_3)_3SiOC)_4Fe_2(CO)_6$

a) Positional parameters

Anisotropic Atoms

Atom	x	y	z
Fe(1)	0.1518(2)	0.3676(2)	0.1687(2)
Fe(2)	0.0698(2)	0.1929(2)	0.3088(2)
Si(1)	0.2327(5)	0.0994(5)	0.0345(4)
Si(2)	0.5181(5)	0.1606(6)	0.2550(5)
Si(3)	0.4154(5)	0.5128(5)	0.2770(5)
Si(4)	0.310(4)	0.3243(5)	0.5585(4)
O(1)	0.2342(9)	0.1187(9)	0.1559(9)
O(2)	0.4127(9)	0.2529(9)	0.1917(9)
O(3)	0.3495(9)	0.3894(9)	0.3346(9)
O(4)	0.1200(8)	0.3670(8)	0.4187(8)

Isotropic Atoms

Atom	x	y	z
O(5)	0.255(1)	0.437(1)	-0.057(1)
O(6)	0.094(1)	0.594(1)	0.179(1)
O(7)	-0.077(1)	0.350(1)	0.091(1)
O(8)	-0.056(1)	0.043(1)	0.214(1)
O(9)	0.116(1)	0.012(1)	0.496(1)
O(10)	-0.153(1)	0.263(1)	0.399(1)
C(1)	0.211(1)	0.194(1)	0.220(1)
C(2)	0.301(1)	0.256(1)	0.239(1)
C(3)	0.270(1)	0.324(1)	0.307(1)

Table (XIX)-Continued

Isotropic Atoms

Atom	x	y	z
C(4)	0.153(1)	0.307(1)	0.347(1)
C(5)	0.211(1)	0.411(1)	0.035(2)
C(6)	0.119(2)	0.504(2)	0.173(2)
C(7)	0.013(2)	0.345(2)	0.133(2)
C(8)	-0.008(2)	0.105(2)	0.249(2)
C(9)	0.126(2)	0.078(2)	0.427(2)
C(10)	-0.071(2)	0.238(2)	0.366(1)
C(11)	0.101(2)	0.169(2)	-0.045(2)
C(12)	0.367(2)	0.158(2)	-0.046(2)
C(13)	0.229(2)	-0.062(2)	0.073(2)
C(14)	0.653(2)	0.221(2)	0.170(2)
C(15)	0.530(2)	0.157(2)	0.407(2)
C(16)	0.487(2)	0.016(2)	0.259(2)
C(17)	0.333(2)	0.623(2)	0.328(2)
C(18)	0.423(2)	0.550(2)	0.122(2)
C(19)	0.561(2)	0.494(2)	0.336(2)
C(20)	0.001(2)	0.237(2)	0.626(2)
C(21)	0.261(2)	0.232(2)	0.601(2)
C(22)	0.134(2)	0.455(2)	0.600(2)

Table (XIX)-Continued

b) Thermal Parameters

Anistropic Atoms

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe(1)	0.0378	0.0643	0.0391	0.0121	-0.0127	-0.0027
Fe(2)	0.0434	0.0585	0.0510	0.0030	-0.0120	-0.0064
Si(1)	0.0720	0.0820	0.0560	0.0124	-0.0174	-0.0288
Si(2)	0.0513	0.1125	0.0625	0.0300	-0.0179	-0.0185
Si(3)	0.0631	0.0819	0.0704	-0.0251	-0.0047	-0.0155
Si(4)	0.0537	0.0721	0.0372	0.0150	-0.0087	00.0002
O(5)	0.0869	0.1111	0.0631	0.0194	0.0110	-0.0050
O(6)	0.1340	0.0630	0.0883	0.0371	-0.0147	-0.0126
O(7)	0.0565	0.1210	0.0963	-0.0058	-0.0343	0.0144
O(8)	0.0996	0.1070	0.1002	-0.0099	-0.0218	-0.0371
O(9)	0.1334	0.0815	0.0914	0.0210	-0.0611	0.0230
O(10)	0.0427	0.0952	0.0973	0.0191	-0.0006	-0.0309

Isotropic Atoms

Atom	U	Atom	U	Atom	U
O(1)	0.0600	C(3)	0.0448	H(1)	constrained
O(2)	0.0583	C(4)	0.0386	↓ H(36)	to have a
O(3)	0.0583	C(5)	0.0532		value of
O(4)	0.0438	C(6)	0.0582		0.1
C(1)	0.0523	C(7)	0.0730		
C(2)	0.0414	C(8)	0.0703		

Table (XIX)-Continued

Isotropic Atoms

Atom	U	Atom	U
C(9)	0.0579	C(16)	0.1187
C(10)	0.0566	C(17)	0.1149
C(11)	0.0904	C(18)	0.1083
C(12)	0.1025	C(19)	0.1095
C(13)	0.1026	C(20)	0.0810
C(14)	0.1244	C(21)	0.0883
C(15)	0.0909	C(22)	0.0745

Table (XX)

Hydrogen Atoms Positions (not refined)

Atom	x	y	z
H(1)	0.113	0.181	-0.126
H(2)	0.084	0.246	-0.032
H(3)	0.031	0.119	-0.016
H(4)	0.355	0.167	-0.127
H(5)	0.432	0.101	-0.018
H(6)	0.382	0.232	-0.034
H(7)	0.301	-0.092	0.045
H(8)	0.219	-0.096	0.157
H(9)	0.159	-0.083	0.037
H(10)	0.644	0.235	0.085
H(11)	0.720	0.169	0.195
H(12)	0.667	0.298	0.179
H(13)	0.614	0.156	0.425
H(14)	0.491	0.229	0.417
H(15)	0.491	0.088	0.459
H(16)	0.547	-0.011	0.212
H(17)	0.484	-0.035	0.337
H(18)	0.408	0.016	0.224
H(19)	0.259	0.645	0.286
H(20)	0.382	0.694	0.311
H(21)	0.316	0.592	0.410
H(22)	0.341	0.561	0.092

Table (XX)-Continued

Atom	x	y	z
H(23)	0.465	0.490	0.097
H(24)	0.463	0.626	0.087
H(25)	0.619	0.490	0.275
H(26)	0.576	0.561	0.363
H(27)	0.562	0.421	0.400
H(28)	-0.046	0.221	0.566
H(29)	0.027	0.161	0.679
H(30)	-0.049	0.280	0.668
H(31)	0.297	0.216	0.532
H(32)	0.316	0.273	0.632
H(33)	0.236	0.159	0.657
H(34)	0.218	0.478	0.598
H(35)	0.097	0.442	0.674
H(36)	0.092	0.519	0.542

Table (XXI)

Structure Amplitudes (x10)

A comparison of Observed and Calculated Structure Amplitudes (x10)

in $((CH_3)_3SiOC)_4Fe_2(CO)_6$

Table (XXI) contains seven pages.

H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL
L = 0**				2	0	232	142	4	8	204	99	-7	-3	281	235
3	-10	164	89	3	0	873	921	7	8	215	198	-6	-3	199	192
2	-9	190	174	4	0	543	514	3	9	171	144	-5	-3	505	476
5	-9	179	166	5	0	284	296	4	9	251	257	-4	-3	184	151
1	-8	277	317	6	0	196	188	5	9	207	229	-3	-3	184	143
2	-8	393	393	10	0	241	213	**L = 1****				-2	-3	317	287
4	-8	150	94	11	0	240	208	-3	-10	251	175	-1	-3	259	89
6	-8	306	311	0	1	408	481	1	-10	237	246	0	-3	227	313
7	-8	241	231	1	1	1350	1387	-5	-9	175	143	1	-3	269	300
1	-7	394	412	2	1	825	673	-3	-9	262	272	2	-3	485	452
2	-7	321	334	4	1	878	874	-2	-9	171	170	3	-3	261	203
3	-7	269	251	7	1	319	332	-1	-9	270	275	4	-3	790	631
4	-7	560	561	8	1	218	223	3	-9	181	172	5	-3	825	785
1	-6	169	185	11	1	201	199	-5	-8	178	187	6	-3	785	758
2	-6	720	663	0	2	416	444	-4	-8	273	297	7	-3	230	235
4	-6	298	294	1	2	385	321	-3	-8	196	213	9	-3	397	359
5	-6	407	395	2	2	143	97	1	-8	173	236	-7	-2	301	311
2	-5	362	317	3	2	432	279	-8	-7	196	116	-6	-2	559	525
3	-5	289	265	4	2	386	402	-7	-7	196	250	-5	-2	534	499
7	-5	320	287	5	2	331	314	-4	-7	205	188	-4	-2	318	238
8	-5	410	438	6	2	611	571	-2	-7	247	293	-3	-2	141	103
9	-5	311	285	7	2	405	376	2	-7	251	213	-2	-2	118	93
1	-4	424	358	8	2	362	388	3	-7	378	359	0	-2	823	859
2	-4	149	133	9	2	524	546	4	-7	192	216	1	-2	479	491
3	-4	291	287	0	3	192	167	5	-7	310	298	2	-2	815	663
4	-4	527	485	1	3	301	262	6	-7	295	313	3	-2	371	231
5	-4	172	174	2	3	886	921	7	-7	269	230	4	-2	1235	1072
6	-4	766	716	3	3	144	138	-9	-6	249	194	6	-2	426	393
8	-4	214	158	5	3	386	382	-8	-6	191	105	7	-2	667	625
9	-4	225	209	6	3	668	634	-6	-6	209	203	-9	-1	229	202
10	-4	297	281	7	3	460	462	-4	-6	167	211	-8	-1	287	266
1	-3	1019	1096	8	3	247	220	-2	-6	439	445	-7	-1	347	363
2	-3	147	148	9	3	294	300	-1	-6	542	548	-4	-1	406	428
3	-3	799	771	10	3	228	229	0	-6	230	270	-3	-1	358	328
4	-3	938	917	0	4	369	376	2	-6	145	134	-2	-1	371	365
5	-3	485	471	1	4	375	402	4	-6	617	617	-1	-1	228	319
6	-3	499	488	2	4	543	521	5	-6	353	338	0	-1	1772	1796
7	-3	517	498	3	4	289	338	-7	-5	302	319	1	-1	669	619
8	-3	209	230	4	4	563	511	-5	-5	192	138	2	-1	402	308
9	-3	285	281	5	4	499	472	-3	-5	294	315	4	-1	650	566
1	-2	864	751	8	4	468	412	-2	-5	324	327	5	-1	411	434
2	-2	387	364	9	4	253	272	0	-5	479	509	8	-1	243	244
3	-2	280	204	0	5	331	359	1	-5	291	299	-11	0	235	215
4	-2	656	598	1	5	724	723	2	-5	383	364	-8	0	185	212
5	-2	1057	1010	2	5	689	721	4	-5	447	425	-7	0	288	327
6	-2	474	438	3	5	385	371	-5	-4	265	226	-6	0	147	147
7	-2	171	160	4	5	182	171	-4	-4	292	285	-5	0	269	274
8	-2	200	251	5	5	500	527	-3	-4	398	410	-4	0	374	399
9	-2	260	241	7	5	394	400	-2	-4	344	313	-3	0	533	537
1	-1	1572	1442	0	6	301	297	-1	-4	513	488	-2	0	155	167
2	-1	1109	971	2	6	135	142	0	-4	392	548	-1	0	743	1025
3	-1	181	162	3	6	640	674	2	-4	365	332	1	0	1506	1459
4	-1	948	915	8	6	206	111	5	-4	255	226	2	0	953	871
5	-1	134	121	0	7	412	444	6	-4	236	192	3	0	131	167
6	-1	126	84	1	7	298	287	7	-4	451	464	4	0	594	573
7	-1	806	802	2	7	399	438	8	-4	256	228	5	0	500	484
8	-1	164	147	3	7	125	181	9	-4	309	258	6	0	309	320
1	0	1085	1180	2	8	156	178	-9	-3	230	200	8	0	203	208

H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL
**L =		1****		6	4	259	205	-4	-9	185	166	-2	-2	438	475
9	0	277	214	7	4	411	374	0	-9	345	404	-1	-2	325	366
11	0	247	222	9	4	320	308	-2	-8	211	201	0	-2	156	144
-9	1	285	329	10	4	181	103	-1	-8	249	274	1	-2	244	208
-6	1	159	151	-9	5	211	190	-6	-7	216	188	2	-2	1128	950
-5	1	525	551	-7	5	222	302	-5	-7	257	336	4	-2	211	193
-4	1	228	150	-6	5	325	320	1	-7	196	203	5	-2	170	179
-3	1	277	365	-4	5	201	191	4	-7	596	606	6	-2	417	388
-2	1	576	578	-2	5	568	584	5	-7	322	333	7	-2	183	196
-1	1	794	927	-1	5	207	211	6	-7	197	190	8	-2	199	191
0	1	1525	1895	0	5	426	423	7	-7	178	190	9	-2	329	373
1	1	175	303	2	5	391	421	-7	-6	305	301	-8	-1	185	140
2	1	399	329	3	5	834	844	-6	-6	243	266	-7	-1	451	498
3	1	1355	1332	4	5	585	551	-4	-6	283	311	-6	-1	445	479
4	1	451	369	6	5	147	155	0	-6	180	178	-5	-1	868	901
6	1	449	403	7	5	242	219	2	-6	234	216	-3	-1	593	590
8	1	408	410	8	5	311	257	4	-6	200	171	-2	-1	1063	1132
9	1	430	409	-8	6	332	356	5	-6	296	262	-1	-1	171	196
-4	2	442	535	-5	6	178	182	6	-6	472	460	0	-1	363	331
-3	2	120	49	-4	6	202	192	7	-6	296	330	1	-1	176	254
-2	2	914	894	-3	6	404	410	-6	-5	220	274	2	-1	412	248
-1	2	735	727	-2	6	230	266	-3	-5	246	198	3	-1	599	321
1	2	239	256	-1	6	344	327	-1	-5	805	771	4	-1	554	535
2	2	360	427	0	6	777	795	0	-5	376	491	5	-1	276	231
3	2	409	405	1	6	252	175	1	-5	214	245	6	-1	206	132
5	2	262	225	2	6	211	267	2	-5	304	296	7	-1	560	554
6	2	466	450	4	6	327	323	3	-5	416	453	8	-1	178	205
7	2	718	689	5	6	178	202	4	-5	421	446	9	-1	398	368
8	2	350	351	6	6	191	215	5	-5	346	379	-9	0	380	470
9	2	210	219	9	6	183	99	-5	-4	177	222	-8	0	453	484
10	2	391	381	-7	7	183	144	-3	-4	170	78	-6	0	295	288
-9	3	220	204	-5	7	226	203	-2	-4	374	321	-4	0	939	880
-8	3	347	363	-3	7	140	117	-1	-4	458	371	-3	0	522	482
-6	3	557	602	-2	7	687	695	0	-4	230	271	-2	0	407	422
-5	3	289	307	-1	7	755	726	1	-4	523	538	-1	0	760	817
-4	3	363	379	1	7	381	349	2	-4	889	837	0	0	921	951
-3	3	541	511	2	7	268	315	3	-4	151	79	1	0	159	146
-2	3	147	228	3	7	297	303	5	-4	234	244	2	0	1493	1441
-1	3	326	246	4	7	318	354	6	-4	432	344	4	0	1029	888
1	3	572	565	8	7	211	185	-6	-3	193	211	5	0	255	359
2	3	710	733	-6	8	259	295	-5	-3	519	479	6	0	325	269
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4	3	455	432	-4	8	338	342	-3	-3	360	338	-7	1	262	265
5	3	172	177	-1	8	503	537	-2	-3	468	451	-6	1	157	197
7	3	361	367	0	8	146	126	-1	-3	176	136	-4	1	591	609
8	3	493	485	1	8	232	199	0	-3	418	595	-3	1	925	810
9	3	588	586	3	8	171	178	1	-3	961	898	-2	1	767	802
-9	4	194	246	5	8	190	186	3	-3	713	646	-1	1	300	320
-8	4	194	242	-6	9	212	242	5	-3	521	398	0	1	158	162
-7	4	343	370	-4	9	169	179	7	-3	344	325	1	1	81	25
-3	4	401	390	-3	9	266	261	8	-3	406	426	2	1	608	624
-2	4	273	253	3	9	200	154	9	-3	291	287	3	1	675	617
-1	4	1202	1109	6	9	191	157	-9	-2	184	149	4	1	618	478
0	4	675	673	7	9	216	209	-8	-2	184	217	5	1	284	273
1	4	223	214	-5	10	192	152	-7	-2	411	403	6	1	341	323
2	4	999	1082	3	10	214	222	-5	-2	278	290	7	1	215	167
4	4	128	100	5	10	221	221	-4	-2	937	874	8	1	170	174
5	4	828	834	**L =		2****		-3	-2	524	475	9	1	215	197

H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL
L = 2**				-3	6	166	172	-5	-4	160	143	-1	0	716	795
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11	1	206	182	-1	6	172	212	-2	-4	515	476	1	0	408	273
-10	2	249	208	0	6	325	297	-1	-4	385	378	2	0	280	263
-8	2	233	250	1	6	601	570	0	-4	417	494	3	0	1148	1074
-6	2	179	183	2	6	260	284	1	-4	488	458	4	0	678	652
-5	2	255	235	3	6	534	515	2	-4	193	169	5	0	144	155
-4	2	154	126	7	6	255	217	3	-4	705	705	6	0	590	583
-3	2	167	244	-8	7	191	169	4	-4	427	426	7	0	675	661
-1	2	825	768	-6	7	240	257	-4	-3	272	262	9	0	215	165
0	2	794	789	-3	7	289	295	-3	-3	446	467	-9	1	183	190
1	2	527	546	-2	7	298	295	-2	-3	178	197	-7	1	148	140
3	2	506	407	0	7	430	490	-1	-3	392	320	-6	1	196	199
4	2	195	174	1	7	163	119	0	-3	501	514	-5	1	173	185
5	2	169	162	3	7	293	313	1	-3	694	591	-4	1	449	440
6	2	184	198	5	7	177	219	2	-3	780	622	-2	1	333	341
7	2	200	202	-4	8	177	127	3	-3	162	123	-1	1	913	906
9	2	418	380	-3	8	154	142	4	-3	210	204	0	1	776	716
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-3	3	501	458	-1	8	365	389	7	-3	178	189	3	1	291	301
-2	3	907	995	2	8	322	348	9	-3	325	358	4	1	563	517
-1	3	168	180	7	8	270	246	10	-3	223	245	5	1	941	894
0	3	340	377	-4	9	209	201	-7	-2	291	274	6	1	183	189
1	3	784	923	-1	9	199	174	-5	-2	424	506	7	1	223	216
3	3	185	214	3	9	259	235	-4	-2	191	196	8	1	314	315
4	3	142	150	-3	10	173	201	-3	-2	372	396	-8	2	177	189
5	3	160	181	-1	10	170	116	-2	-2	703	703	-4	2	328	359
6	3	405	414	1	10	168	111	-1	-2	688	684	-3	2	574	541
9	3	282	266	2	10	228	212	0	-2	647	645	-2	2	971	1157
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-9	4	252	227	-1	-9	328	330	2	-2	648	612	0	2	174	168
-6	4	664	716	3	-9	179	158	3	-2	202	196	1	2	1342	1373
-5	4	201	180	0	-8	320	333	4	-2	342	228	2	2	646	671
-4	4	531	544	3	-8	227	224	5	-2	157	154	3	2	308	312
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-2	4	398	288	-6	-7	243	292	8	-2	408	427	5	2	364	351
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3	4	684	680	2	-7	162	76	-6	-1	251	224	-6	3	470	503
4	4	412	401	6	-7	197	214	-5	-1	239	299	-5	3	368	398
6	4	529	510	-7	-6	195	183	-4	-1	920	945	-4	3	362	387
7	4	304	302	-6	-6	245	259	-3	-1	505	432	-3	3	401	394
8	4	405	362	-5	-6	370	393	-2	-1	287	264	-2	3	483	462
-8	5	302	323	-4	-6	331	327	-1	-1	862	960	-1	3	359	345
-7	5	372	437	-3	-6	234	194	0	-1	456	370	0	3	1033	1091
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-3	5	301	354	3	-6	404	422	4	-1	422	304	4	3	264	256
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2	5	428	432	7	-6	175	178	6	-1	351	334	7	3	159	172
5	5	348	370	8	-6	283	246	8	-1	313	297	8	3	242	218
6	5	151	127	-9	-5	200	131	9	-1	197	240	9	3	301	310
7	5	380	317	-7	-5	303	327	10	-1	277	322	-7	4	442	452
8	5	236	230	-5	-5	182	149	-8	0	311	349	-6	4	159	219
-9	6	189	250	-3	-5	239	283	-7	0	277	338	-4	4	309	288
-6	6	353	370	1	-5	245	268	-6	0	297	279	-3	4	698	757
-5	6	379	411	2	-5	693	650	-4	0	231	213	-2	4	177	190
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H	K	FOBS	FCAL
L = 3**			
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3	4	190	197
5	4	188	207
7	4	396	356
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-6	5	570	561
-5	5	523	520
-4	5	147	147
-3	5	592	582
-2	5	289	290
-1	5	340	311
1	5	116	139
3	5	495	493
4	5	435	480
5	5	172	160
7	5	338	344
8	5	351	325
-9	6	214	237
-8	6	334	396
-6	6	178	179
-5	6	300	277
-4	6	423	426
-3	6	202	229
-1	6	524	490
1	6	138	99
2	6	515	520
4	6	327	357
5	6	243	240
6	6	452	457
7	6	240	222
-8	7	264	280
-6	7	244	238
-3	7	207	207
-1	7	335	359
0	7	368	410
1	7	182	209
2	7	283	290
3	7	769	757
4	7	329	304
5	7	299	344
6	7	177	150
-4	8	234	244
-3	8	313	293
-2	8	364	368
-1	8	305	287
0	8	205	244
1	8	420	454
-3	9	223	208
-2	9	425	417
-1	9	341	320
1	9	265	309
2	9	215	211
4	9	181	158
-4	10	259	220
-3	10	201	164

H	K	FOBS	FCAL
-1	10	175	173
0	10	286	282
-1	11	166	184
L = 4**			
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2	-9	235	237
-3	-8	203	178
-2	-8	304	305
-1	-8	386	369
2	-8	327	343
3	-8	221	244
-5	-7	293	346
-4	-7	319	286
-1	-7	341	314
0	-7	357	383
1	-7	217	241
3	-7	211	225
6	-7	258	289
-7	-6	200	240
-6	-6	299	338
-4	-6	176	142
-3	-6	385	363
-2	-6	335	320
1	-6	246	223
2	-6	216	223
7	-6	269	260
-6	-5	394	409
-5	-5	179	196
-4	-5	324	355
-2	-5	254	246
-1	-5	247	204
1	-5	366	373
3	-5	458	462
4	-5	519	496
5	-5	351	302
8	-5	267	201
-8	-4	225	240
-7	-4	318	284
-4	-4	195	154
1	-4	519	472
2	-4	894	858
3	-4	477	443
5	-4	332	325
7	-4	245	300
-9	-3	287	238
-6	-3	174	154
-4	-3	149	128
-2	-3	289	271
-1	-3	253	256
0	-3	580	585
1	-3	423	383
3	-3	399	404
4	-3	156	156
5	-3	454	438
-9	-2	262	269
-8	-2	174	127
-5	-2	361	362

H	K	FOBS	FCAL
-4	-2	190	201
-3	-2	241	269
-2	-2	448	468
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2	-2	645	606
4	-2	223	164
-7	-1	191	216
-5	-1	292	324
-2	-1	844	854
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1	-1	552	516
2	-1	144	147
4	-1	167	132
5	-1	494	490
7	-1	434	479
9	-1	283	298
-5	0	350	342
-4	0	772	726
-2	0	183	89
-1	0	400	402
0	0	259	109
1	0	603	582
2	0	309	275
5	0	295	349
6	0	407	407
7	0	233	240
10	0	233	224
-7	1	229	244
-6	1	594	579
-5	1	434	411
-3	1	310	333
-2	1	431	432
0	1	862	703
1	1	545	497
2	1	521	581
3	1	665	572
4	1	490	503
6	1	489	501
7	1	397	392
8	1	245	292
9	1	197	137
-8	2	180	216
-6	2	156	132
-4	2	397	372
-2	2	185	185
-1	2	115	111
0	2	397	326
2	2	313	335
3	2	222	225
4	2	426	433
5	2	444	438
6	2	204	181
-8	3	169	200
-4	3	172	142
-3	3	653	642
-2	3	547	555

H	K	FOBS	FCAL
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1	3	419	536
2	3	374	378
3	3	550	585
4	3	215	183
5	3	276	279
7	3	233	222
9	3	218	212
10	3	255	247
-6	4	279	289
-5	4	264	282
-4	4	415	434
-3	4	220	188
-2	4	680	651
-1	4	537	515
0	4	317	317
2	4	176	128
4	4	234	221
8	4	411	451
9	4	249	250
-8	5	170	186
-4	5	392	386
-3	5	138	191
2	5	144	124
3	5	192	209
5	5	220	208
6	5	260	264
7	5	360	377
10	5	214	200
-9	6	178	148
-8	6	182	171
-6	6	281	256
-5	6	183	184
0	6	291	301
2	6	114	60
3	6	663	689
4	6	304	320
5	6	190	199
6	6	243	271
7	6	354	303
9	6	176	140
-8	7	214	182
-5	7	288	292
-2	7	148	186
-1	7	237	165
2	7	258	305
4	7	378	414
5	7	417	410
6	7	323	330
-2	8	330	318
-1	8	311	323
1	8	164	131
2	8	378	392
3	8	280	296
4	8	217	212
-1	9	254	267
0	9	428	417
1	9	270	236

H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL
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4	9	208	217	4	-2	177	142	7	2	422	437	-2	8	180	180
6	9	176	136	5	-2	205	201	8	2	270	245	0	8	194	180
-3	10	265	286	6	-2	381	337	-9	3	170	172	1	8	412	378
-2	10	151	123	-9	-1	211	178	-8	3	288	309	4	8	155	201
-1	10	180	194	-4	-1	941	944	-5	3	187	215	5	8	238	222
**L =	5****			-3	-1	427	451	-4	3	145	130	-4	9	193	133
-1	-8	276	217	-2	-1	562	550	-2	3	280	289	2	9	208	169
0	-8	304	267	-1	-1	473	481	-1	3	107	106	3	9	223	252
-4	-7	188	154	0	-1	383	403	0	3	129	154	4	9	181	121
-2	-7	390	342	1	-1	949	934	2	3	151	101	5	9	158	181
1	-7	245	271	2	-1	188	210	4	3	461	468	4	10	221	195
-5	-6	202	196	3	-1	379	371	5	3	261	269	-3	11	211	204
-2	-6	363	338	4	-1	401	370	7	3	193	186	-1	11	158	85
-1	-6	326	324	5	-1	227	186	9	3	225	174	**L =	6****		
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5	-6	236	230	-7	0	178	193	-3	4	446	472	1	-6	239	251
6	-6	196	205	-6	0	421	469	-2	4	321	307	-4	-5	249	318
-7	-5	270	282	-5	0	331	319	-1	4	401	404	-1	-5	227	219
-4	-5	228	143	-4	0	182	228	1	4	528	552	0	-5	336	354
-3	-5	213	175	-3	0	757	780	2	4	173	183	2	-5	235	228
-2	-5	186	143	-2	0	726	753	3	4	475	496	3	-5	203	118
2	-5	536	528	-1	0	194	209	6	4	283	297	-2	-4	192	221
4	-5	167	200	0	0	261	236	10	4	186	169	1	-4	404	429
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6	-5	295	306	2	0	187	159	-4	5	270	257	4	-4	175	127
7	-5	316	362	5	0	273	262	-2	5	172	181	5	-4	285	282
-6	-4	222	254	7	0	418	463	-1	5	773	755	7	-4	247	293
-5	-4	239	225	8	0	415	438	0	5	433	391	-5	-3	256	242
-3	-4	395	405	9	0	399	416	1	5	335	354	-4	-3	232	233
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3	-4	682	620	-1	1	485	483	-6	6	270	236	6	-3	326	338
4	-4	537	516	0	1	394	305	-5	6	161	174	7	-3	211	241
5	-4	275	283	1	1	708	631	-4	6	305	300	-6	-2	203	182
7	-4	361	396	2	1	362	338	-3	6	322	327	-5	-2	207	204
8	-4	302	351	3	1	591	595	-2	6	311	318	-4	-2	341	353
-8	-3	276	286	4	1	179	174	-1	6	257	288	0	-2	147	185
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6	-3	349	362	-3	2	237	242	-2	7	160	148	2	-1	179	203
-5	-2	270	291	-1	2	393	371	0	7	204	184	3	-1	313	303
-3	-2	354	400	0	2	796	778	1	7	297	331	5	-1	219	171
-2	-2	471	532	1	2	485	433	3	7	231	243	7	-1	284	320
-1	-2	738	721	2	2	488	485	4	7	158	133	-4	0	523	551
0	-2	361	391	3	2	828	851	5	7	360	354	-3	0	320	304
1	-2	152	158	4	2	438	431	6	7	229	178	-2	0	155	200

H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL
L = 6**				-7	6	176	202	5	-2	494	458	1	4	127	118
-1	0	258	256	-6	6	185	211	6	-2	229	240	2	4	242	221
0	0	201	227	-5	6	334	319	7	-2	178	141	3	4	256	260
1	0	406	382	-3	6	180	140	-8	-1	180	148	4	4	209	216
2	0	299	283	-2	6	279	286	-5	-1	226	296	6	4	155	152
3	0	469	412	-1	6	329	310	-2	-1	635	652	8	4	223	214
5	0	511	430	0	6	173	192	1	-1	324	347	-8	5	211	202
9	0	264	279	1	6	306	402	2	-1	351	377	-6	5	207	144
-7	1	167	118	2	6	421	386	3	-1	401	420	-3	5	214	221
-6	1	289	307	5	6	321	308	4	-1	313	262	-1	5	182	195
-4	1	154	171	8	6	181	176	5	-1	264	292	1	5	374	412
-3	1	380	390	9	6	193	192	6	-1	354	333	3	5	335	352
-1	1	560	529	-7	7	161	74	7	-1	227	201	4	5	273	285
0	1	230	216	-6	7	191	226	-7	0	210	196	7	5	161	163
2	1	271	232	-5	7	275	271	-4	0	228	211	-6	6	244	282
3	1	406	410	-4	7	386	355	-2	0	540	548	-4	6	234	251
4	1	562	540	-3	7	425	384	-1	0	616	621	-3	6	335	291
5	1	274	286	3	7	162	148	0	0	360	319	-2	6	218	204
6	1	507	490	5	7	251	228	1	0	441	422	-1	6	161	153
7	1	283	321	6	7	272	265	2	0	372	368	1	6	212	171
8	1	201	278	7	7	230	175	3	0	409	410	3	6	210	212
-8	2	275	293	-2	8	178	187	4	0	155	185	-4	7	265	267
-6	2	218	268	0	8	185	186	5	0	272	219	-2	7	259	263
-5	2	275	288	2	8	245	205	-7	1	191	213	-1	7	404	391
-4	2	190	181	3	8	305	325	-4	1	379	354	8	7	174	181
-3	2	239	241	4	8	242	270	-3	1	155	186	-3	8	292	297
-2	2	255	253	1	9	232	190	-2	1	314	335	0	8	239	259
0	2	153	112	2	9	194	202	-1	1	185	169	4	8	249	247
2	2	186	185	3	9	182	171	0	1	478	446	5	8	200	173
3	2	137	210	4	9	386	405	1	1	428	418	3	9	257	286
4	2	723	737	5	9	206	205	5	1	714	674	5	9	163	139
5	2	749	748	-3	10	206	162	8	1	192	185	-1	10	197	188
8	2	402	438	3	10	214	214	-7	2	207	162	5	10	166	132
-7	3	253	249	**L = 7****				-6	2	389	436	**L = 8****			
-6	3	376	369	0	-6	316	338	-5	2	167	180	-1	-5	283	294
0	3	117	100	1	-6	286	241	-3	2	490	474	0	-5	265	259
1	3	772	773	-3	-5	283	300	-1	2	562	517	-4	-4	228	175
2	3	186	158	-2	-5	366	395	1	2	372	346	-2	-4	400	409
3	3	510	520	-1	-5	192	188	2	2	237	257	0	-4	252	257
6	3	468	472	1	-5	280	313	4	2	255	278	1	-4	335	336
7	3	333	359	3	-5	197	252	5	2	237	204	3	-4	176	140
-3	4	183	208	-4	-4	235	277	6	2	206	221	-6	-3	236	226
-2	4	155	149	-1	-4	658	668	7	2	383	382	-1	-3	242	252
-1	4	443	476	0	-4	235	257	-8	3	301	294	2	-3	276	275
0	4	642	631	-6	-3	209	242	-5	3	496	478	3	-3	196	138
1	4	314	313	-3	-3	303	317	-4	3	298	288	4	-3	194	223
2	4	396	404	-2	-3	493	510	-2	3	151	187	5	-3	313	331
3	4	410	412	1	-3	155	77	-1	3	344	345	-3	-2	203	211
4	4	251	249	2	-3	225	240	0	3	202	182	2	-2	254	253
5	4	248	303	3	-3	177	237	2	3	167	214	5	-2	360	355
-6	5	190	222	5	-3	259	243	3	3	272	289	6	-2	388	428
-4	5	449	443	6	-3	230	240	4	3	276	296	7	-2	251	261
-3	5	151	114	7	-3	238	263	5	3	218	249	-6	-1	173	178
0	5	172	91	-7	-2	168	80	-7	4	209	248	-3	-1	192	211
1	5	629	646	-6	-2	397	445	-6	4	203	181	-1	-1	346	328
2	5	345	338	-5	-2	173	266	-3	4	324	340	0	-1	372	399
7	5	175	191	2	-2	163	165	-2	4	189	197	2	-1	356	360
8	5	163	51	3	-2	424	414	0	4	207	183	3	-1	573	551

H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL
L = 8**				3	5	398	395	-4	2	156	119	4	0	237	253
4	-1	234	256	5	5	252	235	-3	2	316	288	5	0	236	245
5	-1	211	214	6	5	278	305	-2	2	302	303	-4	1	224	178
6	-1	208	235	-7	6	211	215	-1	2	251	231	2	1	170	74
-6	0	176	141	-4	6	251	255	0	2	211	202	3	1	390	371
-5	0	202	184	-2	6	246	276	7	2	178	190	4	1	297	284
-4	0	222	223	-1	6	397	378	-7	3	174	123	5	1	189	180
-3	0	247	233	0	6	173	192	-3	3	339	301	-5	2	184	158
-2	0	435	404	1	6	265	274	-1	3	334	319	-2	2	197	205
0	0	477	459	2	6	206	228	3	3	190	178	-1	2	167	133
1	0	596	649	4	6	413	420	4	3	369	364	0	2	258	240
2	0	196	186	6	6	153	28	5	3	336	315	1	2	234	221
4	0	512	500	7	6	181	178	-5	4	200	209	6	2	207	204
6	0	220	225	-3	7	529	529	-3	4	230	186	-2	3	173	210
-3	1	450	463	-2	7	309	305	2	4	244	233	-1	3	367	375
-2	1	358	362	0	7	432	432	3	4	234	294	0	3	179	160
-1	1	475	447	1	7	403	400	5	4	196	186	2	3	225	264
1	1	384	296	6	7	177	152	6	4	443	455	6	3	230	224
2	1	419	401	-3	8	154	165	-1	5	342	294	-3	4	295	260
3	1	608	604	-2	8	181	202	2	5	196	225	0	4	360	315
4	1	172	169	-1	8	453	441	3	5	223	243	1	4	216	231
5	1	174	161	0	8	261	225	4	5	280	315	5	4	217	234
-5	2	177	189	1	8	145	27	5	5	412	416	-3	5	262	265
-4	2	631	641	2	8	246	262	7	5	200	147	-1	5	198	190
-3	2	210	220	4	8	188	191	-4	6	156	73	6	5	207	215
-1	2	545	546	-4	9	192	175	-2	6	215	201	-4	6	181	171
0	2	180	151	3	9	235	229	0	6	265	256	2	6	175	220
5	2	209	221	**L = 9****				1	6	480	494	-2	7	152	61
7	2	229	267	-1	-4	202	141	2	6	162	150	**L = 11****			
8	2	247	292	-2	-3	270	275	6	6	172	192	0	-1	204	168
-6	3	196	161	1	-3	204	228	-2	7	152	133	1	-1	178	118
-3	3	608	584	-5	-2	193	167	-1	7	365	335	-1	1	181	136
-2	3	558	563	-4	-2	282	258	0	7	223	215	1	1	169	151
0	3	357	355	1	-2	183	170	2	7	283	331	4	1	224	268
3	3	224	235	5	-2	222	216	0	8	275	237	-1	2	245	230
4	3	205	178	-3	-1	287	290	1	8	190	183	2	2	281	325
7	3	209	288	4	-1	242	210	3	8	250	295	3	2	244	242
8	3	233	240	6	-1	181	139	-3	9	205	192	4	2	233	143
-6	4	315	281	-5	0	165	151	**L = 10****				-3	3	167	178
-5	4	231	239	-4	0	170	150	-1	-3	217	169	0	3	263	227
-3	4	202	224	0	0	307	254	1	-3	179	182	1	3	317	344
-2	4	376	382	2	0	242	214	-3	-2	350	371	3	3	160	103
-1	4	147	135	3	0	565	561	-2	-2	221	188	4	3	342	317
1	4	394	413	4	0	213	187	1	-2	278	270	-3	4	318	294
2	4	376	365	-6	1	207	163	-3	-1	167	117	-2	4	183	193
3	4	374	400	-4	1	179	200	-1	-1	276	306	-1	4	205	182
4	4	387	412	-1	1	236	256	4	-1	232	236	0	5	209	178
5	4	468	468	0	1	193	182	5	-1	284	261	-2	6	192	190
-7	5	302	292	1	1	257	247	2	0	215	185	3	6	180	156
-5	5	227	257	2	1	207	181	3	0	246	269	1	7	198	125
2	5	476	503	4	1	364	346								

Table (XXII)

Bond Lengths and their Standard Deviations in $((CH_3)_3SiOC)_4Fe_2(CO)_6$

Atom 1	Atom 2	Distance
Fe(1)	Fe(2)	2.494(4)
Fe(1)	C(5)	1.70(3)
Fe(1)	C(6)	1.72(2)
Fe(1)	C(7)	1.73(2)
Fe(1)	C(1)	2.12(3)
Fe(1)	C(2)	2.20(5)
Fe(1)	C(3)	2.18(5)
Fe(1)	C(4)	2.13(2)
Fe(2)	C(8)	1.77(3)
Fe(2)	C(9)	1.83(4)
Fe(2)	C(10)	1.87(4)
Fe(2)	C(1)	1.93(4)
Fe(2)	C(4)	1.91(3)
C(5)	O(5)	1.19(3)
C(6)	O(6)	1.16(2)
C(7)	O(7)	1.19(2)
C(8)	O(8)	1.15(2)
C(9)	O(9)	1.09(3)
C(10)	O(10)	1.09(2)
C(1)	O(1)	1.41(2)
C(2)	O(2)	1.40(2)
C(3)	O(3)	1.36(2)
C(4)	O(4)	1.36(2)

Table (XXII)-Continued

Atom 1	Atom 2	Distance
Si(1)	O(1)	1.61(2)
Si(2)	O(2)	1.68(4)
Si(3)	O(3)	1.65(4)
Si(4)	O(4)	1.67(2)
Si(1)	C(11)	1.88(4)
Si(1)	C(12)	1.84(4)
Si(1)	C(13)	1.89(1)
Si(2)	C(14)	1.89(5)
Si(2)	C(15)	1.90(1)
Si(2)	C(16)	1.80(1)
Si(3)	C(17)	1.88(3)
Si(3)	C(18)	1.85(2)
Si(3)	C(19)	1.85(3)
Si(4)	C(20)	1.88(5)
Si(4)	C(21)	1.85(4)
Si(4)	C(22)	1.84(1)
C(7)	C(2)	1.38(2)
C(2)	C(3)	1.39(2)
C(3)	C(4)	1.42(2)
C(1)	C(2)	1.38(2)
C(2)	C(3)	1.39(2)
C(3)	C(4)	1.42(2)

Table (XXIII)

Important Bond Angles and their Standard Deviations

in $((CH_3)_3SiOC)_4Fe_2(CO)_6$

Angle reported is that subtended about atom (2) by atoms (1) and (3).

Atom (1)	Atom (2)	Atom (3)	Angle in degrees
Fe(1)	C(5)	O(5)	177(1)
Fe(1)	C(6)	O(6)	177(1)
Fe(1)	C(7)	O(7)	166(1)
Fe(1)	Fe(2)	C(1)	135(1)
C(1)	Fe(2)	C(4)	80(1)
Fe(2)	C(1)	C(2)	116(1)
Fe(2)	C(4)	C(3)	117(2)
Fe(2)	C(8)	O(8)	177(1)
Fe(2)	C(9)	O(9)	176(1)
Fe(2)	C(10)	O(10)	179(1)
C(1)	C(2)	C(3)	114(1)
C(2)	C(3)	C(4)	111(2)
Si(1)	O(1)	C(1)	147(2)
Si(2)	O(2)	C(2)	123(1)
Si(3)	O(3)	C(3)	139(1)
O(1)	Si(1)	C(11)	112(2)
O(1)	Si(1)	C(12)	108(2)
O(1)	Si(1)	C(13)	102(2)
O(2)	Si(2)	C(14)	103(1)
O(2)	Si(2)	C(15)	111(2)
O(2)	Si(3)	C(16)	111(1)

Table (XXIII)-Continued

Atom (1)	Atom (2)	Atom (3)	Angle in degrees
O(3)	Si(3)	C(17)	107(1)
O(3)	Si(3)	C(18)	111(2)
O(3)	Si(3)	C(19)	106(2)
O(4)	Si(4)	C(20)	109(2)
O(4)	Si(4)	C(21)	111(2)
O(4)	Si(4)	C(22)	106(2)

Table (XXIV)

Least Squares Planes through selected Atoms

in $((CH_3)_3SiOC)_4Fe_2(CO)_6$

	Centre of plane (orthogonal coordinates)		
Atoms forming plane	x	y	z
Fe-(C(1)-C(4))	1.8165	4.0076	3.5127
C(1)-O(1)-Si(1)	2.6906	2.0442	1.2980
C(2)-O(2)-Si(2)	5.2043	3.6236	2.7834
C(3)-O(3)-Si(3)	4.3619	6.6698	3.5770
C(4)-O(4)-Si(4)	1.7459	5.9779	5.6419

Best Plane Parameters

Atoms forming plane	Dir. Cos L	Dir. Cos M	Dir. Cos N
Fe-(C(1)-C(4))	0.3834	-0.4912	0.7821
C(1)-O(1)-Si(1)	-0.9319	-0.3058	0.1948
C(2)-O(2)-Si(2)	0.3134	0.8460	0.4314
C(3)-O(3)-Si(3)	-0.7296	0.5864	0.3518
C(4)-O(4)-Si(4)	-0.8979	-0.4252	0.1141

	Angles made by C_n-O-Si plane to FeC_4 plane	
Fe(2)-(C(1)-C(4))	C(1)-O(1)-Si(1)	93°
	C(2)-O(2)-Si(2)	87°
	C(3)-O(3)-Si(3)	107°
	C(4)-O(4)-Si(4)	93°

Chapter Five

The Crystal and Molecular Structure of cis-bis(trimethylsilyl) tetracarbonyl iron.

Introduction

The previous chapter describes the characteristics of a compound formulated as a dimer of bis(trimethylsilyl) tetracarbonyl iron. The original objective of the MacDiarmid reaction[58,59], i.e. the synthesis of bis(trimethylsilyl) tetracarbonyl iron was achieved by reaction of excess $Fe(CO)_5$ with bis(trimethylsilyl) mercury in sunlight[84]. The compound $Fe(CO)_4(Si(CH_3)_3)$ is of interest in that theoretically it could exist in cis or trans forms. It was hoped that the bulky trimethylsilyl substituents would enhance the stability of the cis isomer. A comparative study of the structures of the type cis and trans $Fe(CO)_4(SiX_3)_2$ systems should provide useful data on the cis and trans influence of silyl ligands and hopefully give information towards assessing the importance of dπ-dπ bonding in transition metal to silicon bonds. The spectroscopic properties of $Fe(CO)_4(Si(CH_3)_3)$ in solution (as outlined below) indicate that the major solution species is a cis isomer[84,93].

The infrared spectrum of bis(trimethylsilyl) iron tetracarbonyl shows five carbonyl stretching bands in addition to a shoulder[84]. For a cis isomer of idealised C_{2v} symmetry, only four bands are expected[85]. Conformational splitting of the order of magnitude of 6-7 cm^{-1} has been observed in other cases and may account for the separation of the two pairs of bands at higher frequency[86]. On the other hand some of the

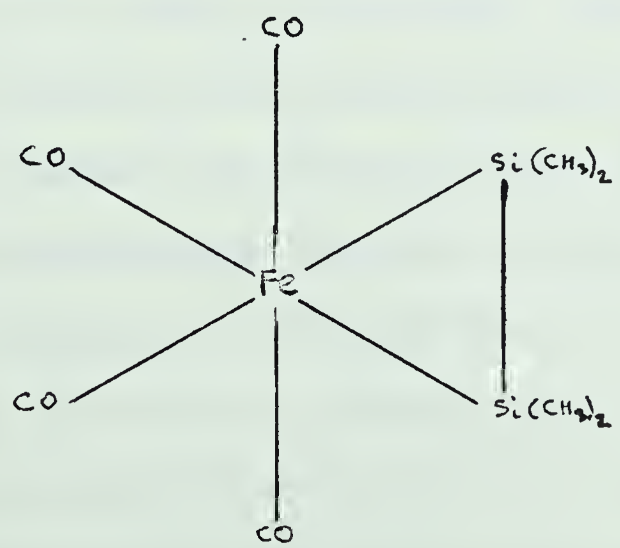
trans isomer may be present in equilibrium as has been observed for $(OC)_4Os(SiMe_3)_2$[87-92].

The C^{13} nmr spectrum of $Fe(CO)_4(Si(CH_3)_3)_2$ determined at -40^oC, in in CD_2Cl_2, showed only one ^{13}C signal in the carbonyl region, at 207.96 ppm. The spectra at -50^oC and -60^oC showed an excessive broadening of the above peak and at -70^oC two separate signals were observed (at 208.34 and 207.53 ppm). No further change in the ^{13}C spectra were observed down to -90^oC[93].

At the present stage, it is difficult to decide whether the non-rigid behaviour of $Fe(CO)_4(SiMe_3)_2$ is due to a cis-trans isomerism, or to a different process which averages out the carbonyls while maintaining the trimethylsilyl groups cis to each other. However, the chemical shift difference between the two ^{13}C signals of the study compound, 0.81 ppm, is close to the value found in the very similar molecule shown below, in Figure (XIII).

Figure (XIII)

A schematic drawing of a cis-$(CO)_4FeX_2$ compound whose NMR spectra has been studied.



The value for the shift difference in this molecule was 1.03 ppm[93]. This indicates that the two ^{13}C resonances in the low temperature spectrum of $Fe(CO)_4(SiMe_3)_2$ are due to the _cis_ compound and do not represent the bands of a _cis-trans_ mixture, which would be accidentally degenerate.

In an attempt to investigate the possible conformers of the compound and hence to elucidate factors involved in the relative stability of _cis_ and _trans_ isomers, a single crystal structure determination was undertaken.

Experimental

Pale yellow prismatic crystals of a size suitable for a single structure determination were kindly supplied by Dr. W.A.G. Graham. Investigation showed the crystals to be unstable in air and of a highly reactive nature. Lindemann glass capilliary tubes (0.3 mm diameter) were taken and the small ends broken off, the broken tube then being immersed in molten candle wax whereupon capilliary action drew a column of wax about 1 cm high into the tube. The tube was withdrawn from the pool of wax and the wax column allowed to solidify. Crystals were then taken from their containers in which, in view of their reactivity, they were stored under nitrogen, and quickly placed into the big ends of the capilliaries and shaken down to the wax seal. A source of localised heat (the tip of a soldering iron) was then applied to the wax column about 0.5 cm from the crystal and a small fraction of the wax melted. Surface tension forces drew a thin layer of molten wax

over the crystals. The wax solidified within seconds of the removal of the heat source, trapping and sealing the crystal in a solid wax coating.

A preliminary diffraction study using a Weissenberg camera led to the assignment of the crystal class as orthorhombic. The systematic absences

$0\,k\,\ell$	$k + \ell = 2n+1$
$h\,0\,\ell$	$h = 2n+1$
$h\,0\,0$	$h = 2n+1$
$0\,k\,0$	$k = 2n+1$
$0\,0\,\ell$	$\ell = 2n+1$

are consistent with space groups $Pna2_1$ (No. 33) or Pnam (a non-standard setting of Pnma, No. 62). The observed density could not be measured by flotation because of the reactive nature of the substance, but the value of 1.32 g/cc calculated on the basis of four formula weights per unit cell seems reasonable for a substance of this type.

Space group $Pna2_1$ has four general positions and the molecule must occupy a general position whereas for Pnam which has eight general positions the molecule would have to occupy a special position of site symmetry $\bar{1}$ or m. Site symmetry $\bar{1}$ is consistent with a trans isomer only, and site symmetry m, although possible for both the cis and trans isomers would require very special constraints placed on the mutual orientation of the trimethylsilyl ligands. Consequently the space group was initially assumed to be the non-centrosymmetric and more general $Pna2_1$.

A careful study of some large, well formed crystals showed that the facial development was limited to faces of the following three forms,

$\{2,0,1\}$ $\{1,1,0\}$ $\{0,0,1\}$

and to a good approximation resembled hexagonal plates with the c axis perpendicular to the plane of the plate. A fresh crystal of dimensions 0.15 mm across the plate and 0.07 mm perpendicular to the plane of the plate was taken and mounted on a Picker Four Circle Automated (FACS) diffractometer and ten reflections were carefully centred in ω, 2θ, χ and ϕ using MoK_α radiation, $\lambda = 0.71069$ Å monochromated by reflection from the 002 plane of a graphite crystal and these values were used to obtain precise cell parameters by least squares methods[48]. These cell parameters were a = 13.360(14), b = 6.640(12) and c = 17.590(18) Å.

A preliminary set of data were collected using the coupled $\omega/2\theta$ scan mode with a 2θ scan range of 2^o plus the $\alpha_1\alpha_2$ dispersion and a 2θ scan speed of 2^o per minute. Background was counted for 20 seconds at both limits of the scan with counter stationary. Three standard reflections were measured every two hours to monitor decomposition effects. Data were collected for all reflections of the type hkl (h, k, l all positive) for which $2\theta < 45^o$. MoK_α radiation was chosen in order to reduce absorption effects. During the collection of a symmetry related octant $(h,\bar{k},l)$ of data rapid and total decomposition of the crystal occurred. The data of the original octant (1217 reflections) were corrected for Lorentz-polarisation and decomposition and the 673 significant observations ($I/\sigma I > 3.0$) used for solution of the structure.

A second data set was collected for a new crystal of dimensions 0.20 mm x 0.10 mm. For this crystal reflections in the octants hkl and $h\bar{k}l$ were measured successfully with only mild monotonic decomposition using the same experimental conditions as for crystal 1. The data from

these two octants of data were merged to give a data set of 710 significant observations. The data from the individual octants were processed separately and a significant observation of the merged data set was defined in terms of $I_{hkl} > 3\sigma I_{hkl}$ and $I_{hk\bar{l}} > 3\sigma I_{hk\bar{l}}$. This extreme definition of significance which corresponds approximately to $I_{merged} > 4.2\sigma I_{merged}$, was considered necessary in view of spurious pulses that were being detected by the counter at this particular time. Previous observations of similar random pulses have been traced to the operation of Tezler coils using the same power line. In this case the source of the pulses may have been the newly installed paging system in a nearby building[94]. The gross non-equivalence of $|F_{hkl}|$ and $|F_{hk\bar{l}}|$ was used in detecting six reflections which appeared to suffer from spurious pulses. Data from the two crystals were not merged because the decomposition correction for crystal 1 were excessive. Also, since the space group was possibly $Pna2_1$, data from the two crystals need not have been equivalent due to the effects of anomalous scattering, i.e. one data set could correspond to hkl and the other data set to $hk\bar{l}$ and this averaging is not valid when the diffraction symmetry is mm2. This second data set was used for refinement of the structure.

Solution and Refinement of the Structure

A three dimensional Patterson map[49] was calculated and the peaks compared with the vector distribution expected for the two space groups. The observed vector distribution corresponded to a Pnam solution with the two silicon atoms related by the mirror plane as in the case of

$(h^5\text{-}C_5H_5)Fe(CO)H(SiF_2CH_3)_2$. An electron density difference map calculated from the structure factors phased by the silicon and iron atoms (R = 25%) showed the four carbonyl peaks. The remaining carbon atoms were located in a subsequent electron density difference map. Refinement of the iron, silicon, carbon and oxygen atoms was carried out in space group Pnam with expectation that anomalous thermal parameters would indicate any deviations from exact mirror symmetry. The least squares refinement of all atoms with anisotropic thermal parameters converged to R1 = 7.5% and no anomalous thermal parameters materialised. An electron density difference map was calculated and nine of the highest fifteen peaks appeared to correspond to reasonable positions for the methyl hydrogen atoms. However, the two largest peaks at

$$x = -0.18 \qquad y = 0.10 \qquad z = 0.25$$

and

$$x = -0.09 \qquad y = 0.00 \qquad z = 0.36$$

were unexplained and alarmingly close to the iron and silicon positions. The recognition that these two peaks were separated by a distance corresponding to an iron-silicon bond (2.4 to 2.5 Å) promoted an extremely careful examination of the difference map. The remaining four unassigned peaks of the 15 largest and other peaks among the top thirty peaks appeared to correspond to a ghost molecule related by a two-fold axis (corresponding to the line x = -0.12, y = 0.05, z) to the molecule previously located. This particular ghost image would not be expected to arise from a slight deviation of mirror symmetry i.e. the true space group being $Pna2_1$, but approximately Pnam. This disorder was assumed to occur in about five percent of the molecules and was allowed for in

structure factor calculations in which the predominant molecule was given as an occupancy factor of 95%. The term predominant molecule follows from Hanson[95]. Hydrogen atoms were included as hindered rotors and one cycle of least squares refinement reduced R1 to 3.3% from the previous value of 7.5%. Two more cycles of refinement were computed and the positional parameters of the iron and silicon atoms in the alternate molecule allowed to vary. An electron density difference map phased on the entire predominant molecule and the heavy atoms in the alternate molecule led to a peak corresponding to 0.3 e/Å^3 for the position ascribed to the 5% alternate iron atom. The peak in the electron density difference map originally computed was 1.8 a/Å^3. A value of 6% was therefore taken for the measure of the disorder and two more cycles of full matrix least squares computed, reducing R1 to its final value of 2.9%. The 6% alternate atoms were all relocated by assuming the new path of the two-fold disorder which best fitted the refined positions of the heavy atoms, iron and ilicon, in both molecules. This axis passed through the point-0.1208, 0.0552 in x and y respectively. At this point the data were transformed to the standard space group, Pnma (no. 62) and all data in tables are consistent with this space group. The new unit cell becomes a = 13.360(14), b = 17.590(18), c = 6.640(12) Å.

Results and Conclusions

The structural determination shows that the molecule is a cis isomer and that it is grossly distorted from ideal octahedral geometry. A per-

spective view of the molecule is shown in Figure (XIV) overleaf. Table (XXV), following Figure (XIV) lists atomic parameters for the predominant molecule. The next table (XXVI) lists those for the alternate molecule. Following this, Tables (XXVII) and (XXVIII) list the bond distances and angles and their standard deviation, respectively, for the predominant molecule. Table (XXIX) lists non-bonding intramolecular distances and Table (XXX) lists structure amplitudes. The packing diagram, Figure (XV) viewed down the y axis, shows no obvious cause for the severe distortion from octahedral geometry in terms of "packing forces". Figure (XVI) shows a view down the y axis of a single molecule, with other atoms drawn to the scale of their van der Waals radii. The reason for the disorder is apparent from this figure, and Figure (XVII), obtained by rotating Figure (XVI) by 90^{o} about the projection of the iron silicon bond onto the mirror plane.

Figure(XIV)

A perspective view of the cis-bis(trimethylsilyl) iron tetracarbonyl molecule

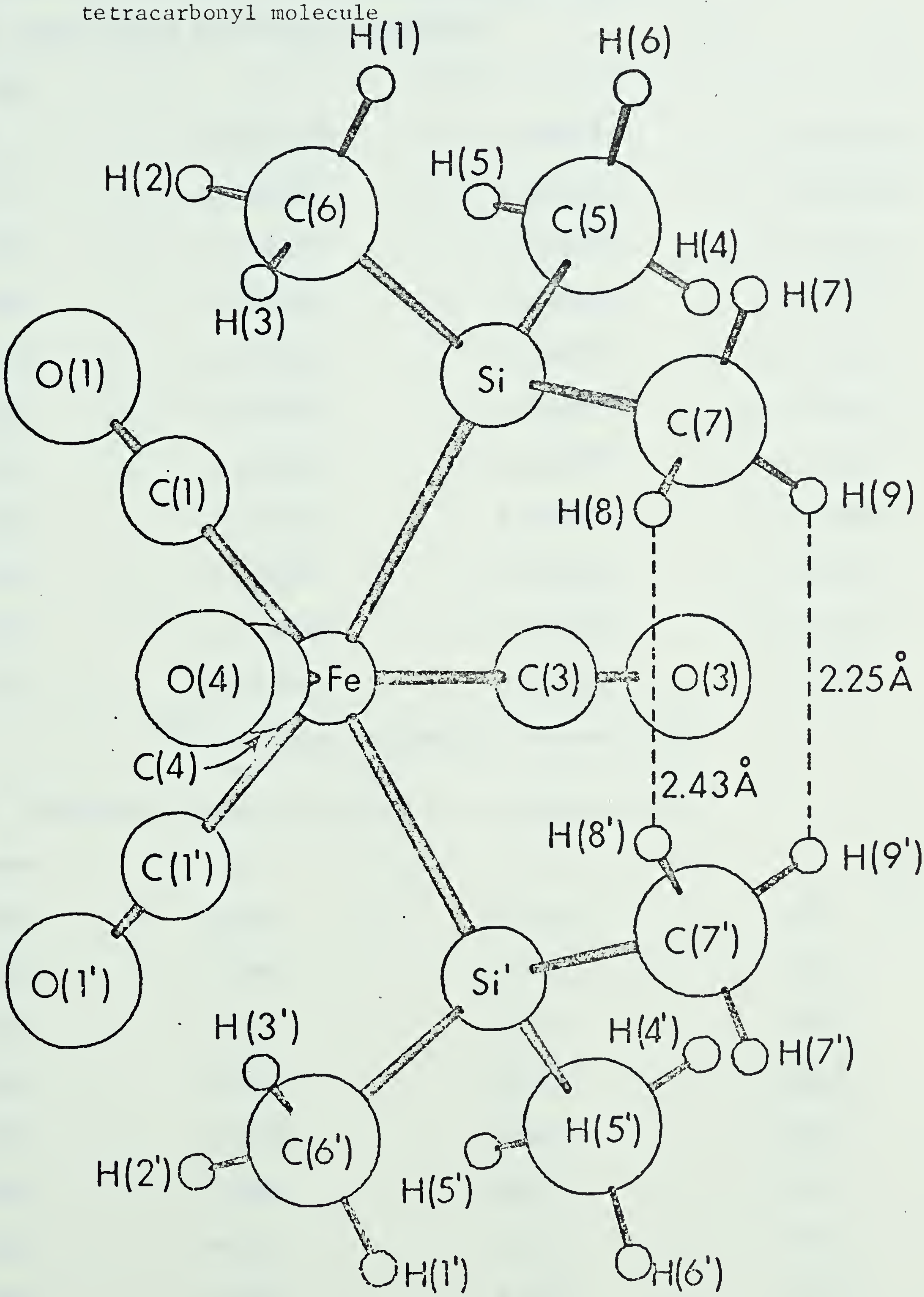


Table (XXV)

Atomic and group parameters for the predominant molecule $(CO)_4Fe(Si(CH_3)_3)_2$ with standard deviations in parenthesis.

a) Heavy Atoms Positional Parameters

Atom	x	y	z
Fe	-0.0611(1)	0.2500xx	-0.0170(1)
Si	-0.1488(1)	0.3656(1)	0.0920(2)
C(1)	0.0193(3)	0.3218(3)	-0.120(1)
O(1)	0.0713(2)	0.3654(2)	-0.191(1)
C(3)	-0.1650(5)	0.2500xx	-0.179(1)
O(3)	-0.2333(4)	0.2500xx	-0.287(1)
C(4)	-0.0302(4)	0.2500xx	0.243(1)
O(4)	-0.0119(4)	0.2500xx	0.412(1)
C(5)	-0.0676(4)	0.4226(3)	0.263(1)
C(6)	-0.1779(4)	0.4274(3)	-0.126(1)
C(7)	-0.2699(3)	0.3478(3)	0.222(1)

xx constrained by symmetry considerations.

b) Hydrogen Coordinates derived from hindered rotor

Atom	x	y	z
H(1)	-0.101	0.474	0.283
H(2)	-0.000	0.432	0.196
H(3)	-0.062	0.394	0.385
H(4)	-0.224	0.401	-0.222
H(5)	-0.1126	0.439	-0.202
H(6)	-0.208	0.477	-0.080
H(7)	-0.303	0.396	0.251
H(8)	-0.255	0.319	0.352
H(9)	-0.314	0.314	0.135

Table (XXV)-Continued

c) Thermal parameters for the Predominant Molecule

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe	0.0305	0.0385	0.0565	0.0000	0.0026	0.0000
Si	0.0405	0.0359	0.0808	0.0036	0.0046	0.0004
C(1)	0.0385	0.0575	0.0715	0.0005	0.0079	0.0064
O(1)	0.0615	0.0751	0.1274	-0.0137	0.0297	0.0246
C(3)	0.0572	0.0501	0.0674	0.0000	-0.0016	0.0000
O(3)	0.0767	0.0898	0.1051	0.0000	-0.0457	0.0000
C(4)	0.0380	0.0410	0.0719	0.0000	0.0042	0.0000
O(4)	0.0855	0.0779	0.0582	0.0000	-0.0110	0.0000
C(5)	0.0838	0.0534	0.1378	0.0015	-0.0094	-0.0293
C(6)	0.0753	0.0582	0.1204	0.0126	-0.0015	0.0194
C(7)	0.0629	0.0548	0.1336	0.0099	0.0387	-0.0062

d) Hindered Rotor Parameters for the Methyl Hydrogens

Ring No.	x	y	z	B	Bd	Radius
1	-0.054	0.4337	0.288	10	4	0.95
2	-0.182	0.4390	-0.168	10	4	0.95
3	-0.291	0.3430	0.2457	10	4	0.95

	D	E	F
1	2.596	0.715	4.225
2	0.627	0.249	4.192
3	6.115	2.081	1.157

Table (XXVI)

Positional Parameters for the Alternate Molecule, $(CO)_4Fe(Si(CH_3)_3)_2$

Parameters not refined.

Atom			
Fe	-0.180	0.250	0.128
Si	-0.094	0.136	0.015
C(1)	-0.261	0.178	0.231[xx]
O(1)	-0.313	0.135	0.302
C(3)	-0.077	0.250	0.290
O(3)	-0.008	0.250	0.398[xx]
C(4)	-0.211	0.250	-0.132
O(4)	-0.229	0.250	-0.301[xx]
C(5)	-0.174	0.077	-0.153[xx]
C(6)	-0.063	0.073	0.237[xx]
C(7)	0.028	0.152	-0.111

[xx]denotes near coincidence with an atom in the predominant orientation.

Table (XXVII)

Bond Distances and their Standard Deviation for the Predominant Molecule

$(CO)_4Fe(Si(CH_3)_3)_2$

Atom 1	Atom 2	Distance in Angstroms
Fe	C(1)	1.793(5)
Fe	C(3)	1.756(7)
Fe	C(4)	1.775(7)
Fe	Si	2.456(2)
Si	C(5)	1.853(6)
Si	C(6)	1.852(6)
Si	C(7)	1.866(5)
C(1)	O(1)	1.137(6)
C(3)	O(3)	1.160(9)
C(4)	O(4)	1.143(9)

Table (XXVIII)

Bond Angles and their Standard Deviations for the Predominant Molecule

$(CO)_4Fe(Si(CH_3)_3)_2$

Angle reported is that subtended about Atom 2 by Atom 1 and Atom 3.

Atom 1	Atom 2	Atom 3	Angle
C(3)	Fe	C(4)	141.2(1)
C(1)	Fe	C(1')	89.5(4)
C(1)	Fe	C(3)	103.9(3)
C(1)	Fe	C(4)	103.4(2)
C(1)	Fe	Si	79.3(2)
Si	Fe	C(3)	78.7(2)
Si	Fe	C(4)	79.9(2)
Si	Fe	Si'	111.8(1)
Fe	Si	C(5)	110.3(2)
Fe	Si	C(6)	110.8(2)
Fe	Si	C(7)	114.4(2)
C(5)	Si	C(6)	106.4(2)
C(5)	Si	C(7)	108.3(3)
C(6)	Si	C(7)	106.2(3)
Fe	C(1)	O(1)	177.4(5)
Fe	C(3)	O(3)	179.6(4)
Fe	C(4)	O(4)	178.8(4)

Table (XXIX)

Non-Bonding Intramolecular Distances in $(CO)_4Fe(Si(CH_3)_3)_2$

Atom 1		Atom 2	Distance
Si	-	C(1)	2.759(7)
Si	-	C(3)	2.724(5)
Si	-	C(4)	2.766(3)
Si	-	Si	4.067(3)
C(1)	-	C(1')	2.53(1)
C(1)	-	C(3)	2.795(7)
C(1)	-	C(4)	2.797(7)
H(8)	-	H(8)	2.43
H(9)	-	H(9)	2.25
C(7)	-	C(7')	3.437(7)

Table (XXX)

Structure Amplitudes

A Comparison of the Observed and Calculated Structure Amplitudes (x10) for $(CO)_4Fe(Si(CH_3)_3)_2$

Table (XXX) contains four pages.

H	K	FOBS	FCAL
L = 0**			
0	4	282	270
0	6	1186	1136
0	8	1499	1501
0	10	1425	1416
0	12	542	536
0	14	90	70
0	16	630	614
0	18	573	576
2	0	696	655
2	1	1535	1543
2	2	765	725
2	4	772	730
2	5	1073	1004
2	6	623	607
2	7	958	946
2	8	289	290
2	9	706	704
2	10	214	224
2	11	499	511
2	12	355	358
2	14	380	380
2	15	175	181
2	16	233	233
2	17	466	488
2	18	107	109
4	0	246	233
4	1	181	181
4	2	734	703
4	3	1015	972
4	4	796	783
4	5	1125	1094
4	6	150	156
4	7	412	424
4	8	263	261
4	9	78	83
4	11	435	430
4	12	468	455
4	13	577	566
4	14	344	342
4	15	218	214
4	16	85	101
4	18	129	129
6	0	77	80
6	1	178	180
6	2	201	198
6	3	868	844
6	4	338	338
6	5	1321	1305
6	6	281	283
6	7	558	558
6	8	155	160
6	10	119	121
6	11	427	425
6	12	265	262
6	13	478	488
6	14	172	171
6	15	193	195

H	K	FOBS	FCAL
8	0	510	514
8	1	506	498
8	2	258	255
8	3	178	173
8	4	409	408
8	5	273	269
8	6	630	639
8	7	287	284
8	8	271	263
8	9	496	503
8	10	254	258
8	11	111	113
8	12	334	341
8	13	228	225
8	14	170	166
10	0	677	688
10	1	281	284
10	2	341	344
10	3	156	147
10	5	231	231
10	6	196	196
10	8	517	522
10	10	365	368
10	11	264	264
10	13	186	185
12	0	181	181
12	1	436	440
12	3	168	172
12	4	111	112
12	7	237	241
12	9	288	287
12	10	90	66
14	0	280	291
14	1	118	116
14	2	107	121
14	3	176	172
14	4	85	91
L = 1**			
0	1	101	144
0	3	441	428
0	5	310	301
0	9	124	121
0	13	182	177
0	15	137	136
1	0	1648	1677
1	1	855	898
1	2	745	762
1	3	208	183
1	5	61	51
1	6	250	258
1	7	363	373
1	8	637	643
1	9	515	506
1	10	577	583
1	11	230	228
1	12	173	178
1	13	122	125
1	14	143	145

H	K	FOBS	FCAL
1	16	359	354
1	17	269	275
1	18	265	266
2	0	627	612
2	1	125	129
2	2	126	71
2	3	298	300
2	4	735	715
2	5	1370	1322
2	6	267	263
2	7	503	484
2	8	317	315
2	9	178	168
2	10	117	112
2	11	152	157
2	12	244	234
2	13	162	167
2	14	187	189
2	18	117	115
3	0	528	525
3	1	647	638
3	2	313	296
3	3	763	730
3	4	563	558
3	5	568	564
3	7	589	591
3	8	302	294
3	9	568	578
3	10	133	137
3	11	337	344
3	12	309	307
3	13	183	191
3	14	339	337
3	15	241	240
3	17	240	239
3	18	100	111
4	0	1243	1186
4	3	97	96
4	4	230	216
4	5	177	176
4	6	275	251
4	8	78	76
4	11	157	149
4	12	195	197
4	13	110	110
4	17	95	86
5	0	234	226
5	1	111	103
5	2	401	389
5	3	914	894
5	4	214	216
5	5	904	892
5	6	212	219
5	7	288	286
5	8	418	420
5	9	69	62
5	10	218	228
5	11	324	314

H	K	FOBS	FCAL
5	13	500	501
5	14	79	69
5	15	198	205
6	0	110	104
6	1	245	253
6	3	175	160
6	4	141	135
6	5	170	161
6	6	95	98
6	7	328	329
6	8	136	146
6	9	479	475
6	10	77	92
6	11	80	78
6	12	89	74
6	13	127	135
6	14	79	85
6	17	91	90
7	0	103	112
7	1	307	304
7	2	429	435
7	3	97	108
7	4	820	823
7	5	256	259
7	6	602	599
7	7	276	276
7	8	212	210
7	9	236	234
7	10	192	190
7	11	190	191
7	12	395	389
7	14	337	326
7	16	100	88
8	0	384	395
8	1	196	196
8	2	235	237
8	3	92	88
8	4	116	125
8	5	177	181
8	6	106	109
8	7	112	107
8	8	182	191
8	9	242	237
8	10	142	147
8	13	105	99
9	0	711	714
9	2	478	480
9	3	331	333
9	4	284	291
9	5	367	368
9	6	407	410
9	8	497	493
9	9	129	133
9	10	421	418
9	11	157	165
9	12	182	188
9	13	265	263
9	14	98	108

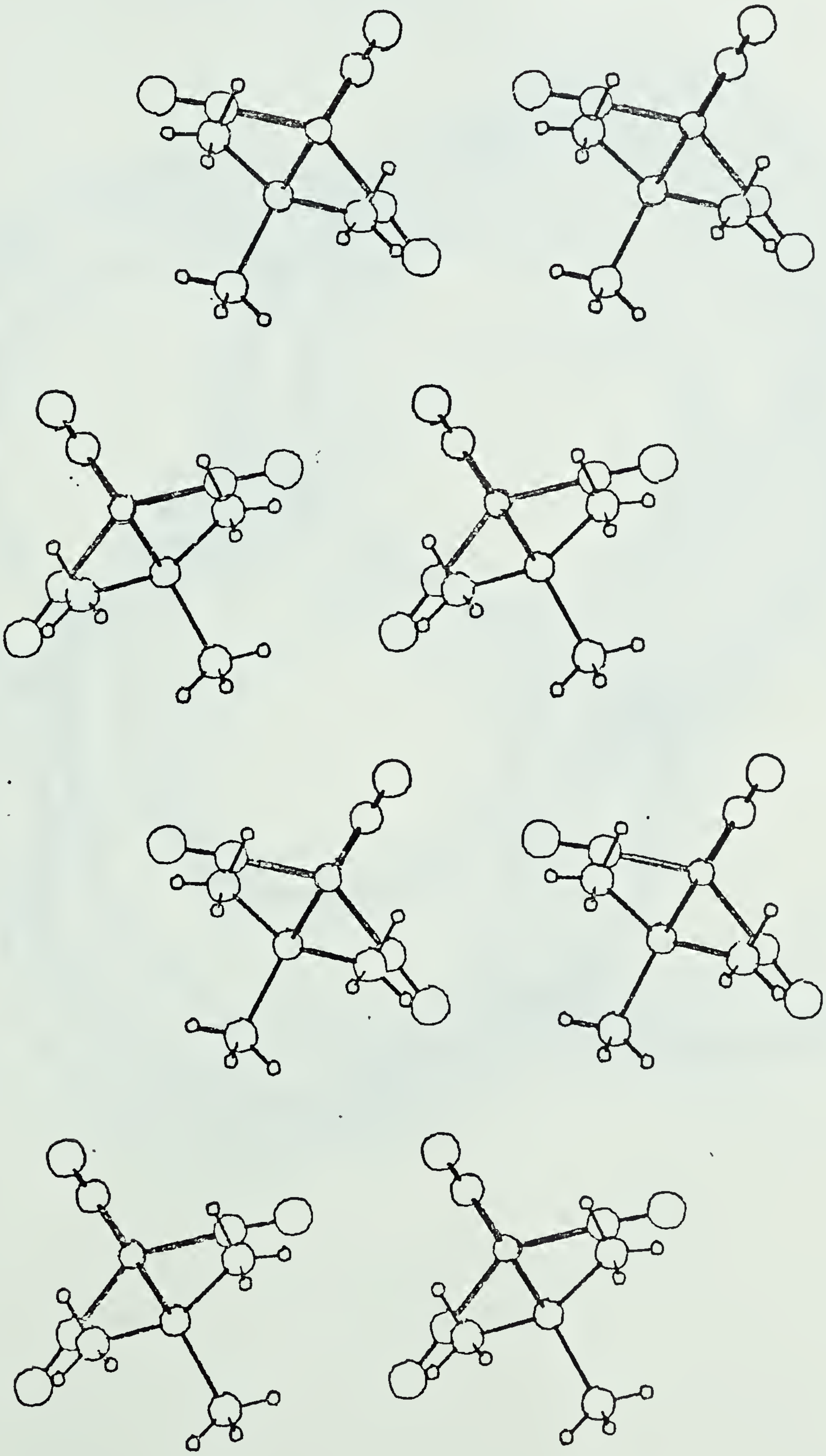
H	K	FOBS	FCAL
L = 1**			
10	1	81	93
10	3	190	191
10	4	156	158
10	5	227	223
10	13	118	114
11	0	226	214
11	1	486	496
11	2	161	164
11	3	233	242
11	5	137	140
11	6	97	88
11	7	260	256
11	8	224	231
11	9	333	333
11	10	123	126
11	11	193	210
12	2	151	161
12	4	238	251
13	0	220	221
13	1	298	309
13	3	208	217
13	4	117	114
13	5	115	119
13	7	168	172
L = 2**			
0	0	261	273
0	2	529	530
0	4	614	631
0	6	260	273
0	8	497	506
0	10	275	285
0	14	244	237
0	16	246	247
0	18	153	146
1	0	358	352
1	1	586	614
1	2	274	287
1	3	262	290
1	4	552	569
1	5	341	342
1	6	440	421
1	8	450	441
1	9	96	92
1	10	188	196
1	11	210	205
1	12	275	283
1	13	310	303
1	14	147	147
1	15	116	111
1	18	96	98
2	0	572	569
2	1	660	669
2	2	819	850
2	3	261	261
2	4	619	638
2	5	224	208
2	6	358	367
2	7	347	364
2	8	407	413
2	9	619	626
2	10	352	359
2	11	152	155
2	12	331	334
2	14	272	271
2	15	146	140
2	16	90	95
2	17	180	177
2	18	80	75
3	0	227	215
3	1	698	676
3	2	170	161
3	3	132	130
3	4	546	540
3	5	508	500
3	6	314	318
3	7	207	202
3	9	471	481
3	12	218	221
3	13	126	134
3	14	149	137
3	17	168	171
4	0	428	406
4	1	597	575
4	2	188	176
4	3	814	800
4	4	234	228
4	5	483	492
4	6	86	85
4	7	549	544
4	8	197	195
4	9	504	505
4	10	147	147
4	11	284	278
4	13	306	299
4	15	262	264
4	17	138	139
5	0	247	254
5	1	180	166
5	2	120	119
5	4	222	223
5	7	128	135
5	8	422	420
5	9	121	121
5	10	170	176
5	12	156	162
5	14	97	104
5	16	102	89
6	0	165	162
6	1	315	314
6	2	287	282
6	3	341	344
6	4	598	584
6	5	224	226
6	6	367	358
6	7	196	195
6	8	133	134
6	9	246	246
6	11	184	191
6	12	217	206
6	13	187	187
6	14	269	273
6	15	137	124
6	16	96	104
7	1	297	298
7	3	360	368
7	4	153	138
7	5	394	395
7	6	241	240
7	7	206	210
7	9	356	356
7	12	76	67
7	13	237	243
8	0	273	278
8	2	468	469
8	3	70	56
8	4	535	539
8	6	318	315
8	8	279	271
8	10	270	273
8	12	254	258
8	13	84	77
8	14	243	236
9	0	301	317
9	3	81	80
9	4	213	221
9	5	266	269
9	6	77	78
9	7	87	90
9	9	85	84
9	13	91	97
10	0	236	229
10	1	240	248
10	2	208	206
10	3	256	254
10	4	131	139
10	5	184	178
10	6	132	140
10	7	208	212
10	8	211	213
10	9	230	229
10	10	154	158
10	11	120	115
11	1	160	162
11	3	117	120
11	4	239	235
11	5	94	101
11	8	150	161
11	9	85	81
12	1	342	351
12	3	184	189
12	7	217	216
12	9	296	297
13	3	104	105
13	4	88	98
13	5	123	125
L = 3**			
0	1	141	149
0	3	66	60
0	5	450	460
0	7	257	260
0	9	454	456
0	11	217	220
0	13	346	340
1	0	135	132
1	1	130	138
1	2	370	412
1	3	241	255
1	4	563	621
1	5	115	112
1	6	467	478
1	7	141	148
1	8	314	323
1	9	143	143
1	10	232	239
1	12	279	277
1	14	202	205
1	15	85	85
2	0	204	205
2	1	249	260
2	2	90	82
2	3	146	154
2	4	438	478
2	5	139	130
2	6	303	314
2	7	130	126
2	8	287	296
2	10	81	73
2	11	84	73
2	12	271	280
2	13	90	77
2	14	140	129
2	15	97	101
2	17	108	111
3	0	267	268
3	1	603	617
3	2	154	156
3	3	220	231
3	4	222	228
3	5	188	197
3	6	366	377
3	7	347	371
3	8	235	242
3	9	344	346
3	10	178	184
3	11	262	254
3	12	129	131
3	13	191	182
3	15	143	136
3	16	99	96
4	0	587	557
4	1	307	290

H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL
L = 3**				9	6	182	175	3	2	126	127	10	4	269	260
4	2	248	238	9	7	151	144	3	4	134	130	10	5	83	70
4	3	295	292	9	8	127	118	3	6	109	120	10	6	198	186
4	4	114	115	9	9	165	170	3	7	161	165	10	7	122	120
4	5	526	522	9	10	101	103	3	8	95	100	11	4	115	99
4	6	114	125	9	12	153	147	3	9	246	254	11	5	98	101
4	8	394	391	10	0	233	234	3	11	95	91	**L = 5****			
4	9	207	210	10	1	117	111	4	0	214	197	0	3	183	198
4	10	276	272	10	2	85	73	4	1	587	581	0	5	132	148
4	13	174	169	10	3	192	198	4	3	215	212	0	7	90	77
5	0	179	167	10	5	269	266	4	4	155	142	1	0	169	158
5	1	725	709	10	9	125	122	4	5	320	316	1	2	254	265
5	2	120	114	11	0	182	179	4	7	337	341	1	3	188	196
5	3	363	358	11	1	179	182	4	8	211	210	1	4	345	369
5	4	200	195	11	2	150	150	4	9	292	286	1	5	187	176
5	5	367	361	11	3	159	156	4	10	139	128	1	6	290	306
5	6	189	192	11	4	130	133	4	11	291	289	1	8	194	205
5	7	448	450	11	5	155	159	4	13	135	141	1	10	151	166
5	9	375	373	11	6	111	114	4	14	94	80	1	12	174	165
5	11	286	279	11	7	196	195	5	0	543	521	1	13	155	152
5	12	151	148	11	9	170	166	5	1	84	49	2	2	92	93
5	13	192	195	12	4	185	193	5	2	275	260	2	4	123	114
5	14	102	101	12	6	96	87	5	6	100	103	3	0	363	351
5	15	187	192	13	1	147	149	5	8	367	369	3	1	202	185
6	0	327	318	**L = 4****				5	10	266	255	3	2	130	133
6	1	303	297	0	0	101	112	6	0	608	601	3	3	310	325
6	4	138	136	0	2	283	306	6	1	366	340	3	5	327	330
6	5	97	101	0	4	495	528	6	2	303	297	3	6	115	110
6	6	116	118	0	6	403	416	6	3	200	192	3	7	164	164
6	7	210	215	0	8	209	213	6	5	141	132	3	8	254	266
6	9	272	297	0	10	211	212	6	6	152	156	3	9	100	102
6	10	149	147	0	12	305	295	6	7	200	199	3	10	191	191
6	13	90	96	0	14	189	189	6	8	216	208	3	11	159	157
7	0	472	472	1	2	85	86	6	9	219	209	3	13	184	176
7	1	96	76	1	3	340	384	6	10	268	260	4	0	157	163
7	2	415	418	1	4	200	225	6	11	136	131	4	2	128	126
7	3	143	139	1	5	371	395	6	12	148	140	4	8	103	114
7	4	357	348	1	6	77	74	7	1	190	176	5	0	145	133
7	6	293	286	1	11	133	142	7	3	101	90	5	1	348	339
7	8	243	245	1	12	97	106	7	4	101	100	5	2	84	72
7	10	265	261	1	13	203	197	7	6	83	71	5	7	165	163
7	12	242	241	1	14	92	82	7	7	141	142	5	9	263	250
7	14	162	162	1	15	104	101	7	9	164	170	5	11	134	125
8	0	263	272	2	0	260	262	8	0	314	306	6	1	157	151
8	1	199	191	2	1	105	106	8	2	252	247	6	2	82	68
8	4	245	247	2	3	332	361	8	3	156	154	6	3	123	121
8	5	223	221	2	4	183	207	8	4	156	150	6	5	100	96
8	6	127	131	2	5	364	369	8	5	99	97	7	0	295	292
8	7	214	217	2	6	326	350	8	6	156	155	7	1	117	103
8	8	144	145	2	7	131	127	8	8	203	202	7	2	148	135
8	9	116	101	2	8	238	248	8	9	94	100	7	3	168	172
8	10	80	75	2	10	200	206	8	10	175	164	7	5	140	128
8	11	90	84	2	11	145	145	9	0	179	171	7	8	211	205
8	12	110	115	2	12	112	116	9	3	103	92	8	1	124	114
9	0	131	125	2	13	248	241	9	4	111	124	8	3	125	122
9	1	126	131	2	15	120	116	9	8	112	108	9	0	132	130
9	2	229	221	3	0	87	80	10	0	155	146	9	2	175	170
9	4	267	265	3	1	335	348	10	2	197	197	9	4	193	182

H	K	FOBS	FCAL
**L =		5****	
9	6	139	128
0	2	98	105
0	4	209	220
0	6	145	147
1	1	96	97
1	7	125	132
1	9	127	123
2	3	181	190
2	5	177	195
2	8	93	84
3	0	165	150
3	5	87	78
3	6	106	93
4	1	149	142
4	4	108	112
5	1	101	82
5	4	102	107
6	0	191	171
6	1	146	126
6	2	106	98
7	1	99	87
**L =		7****	
1	0	103	91
1	2	116	102
2	0	141	134

Figure(XV)

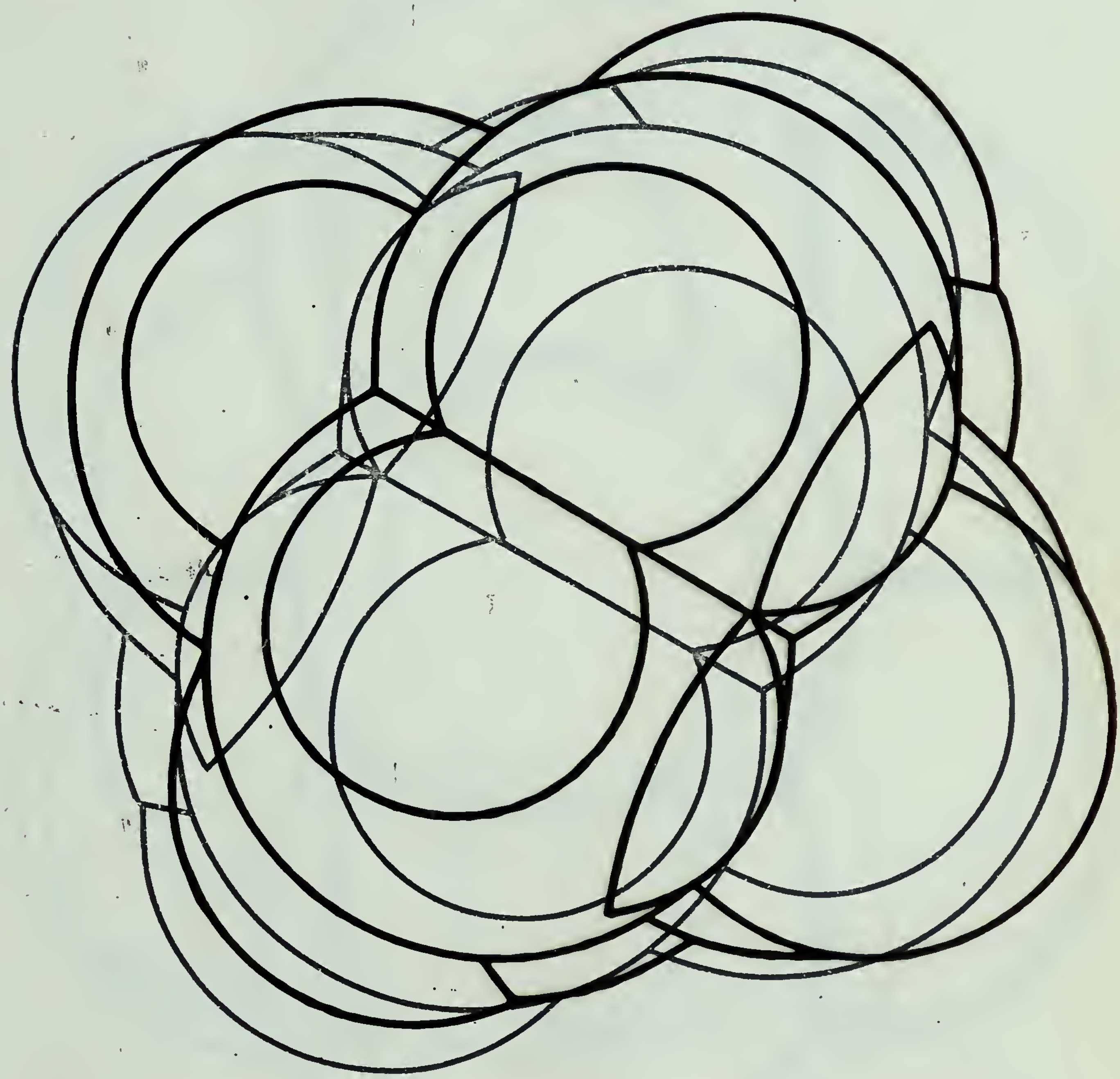
A packing diagram of cis-bis(trimethylsilyl) iron tetracarbonyl seen down the b axis.

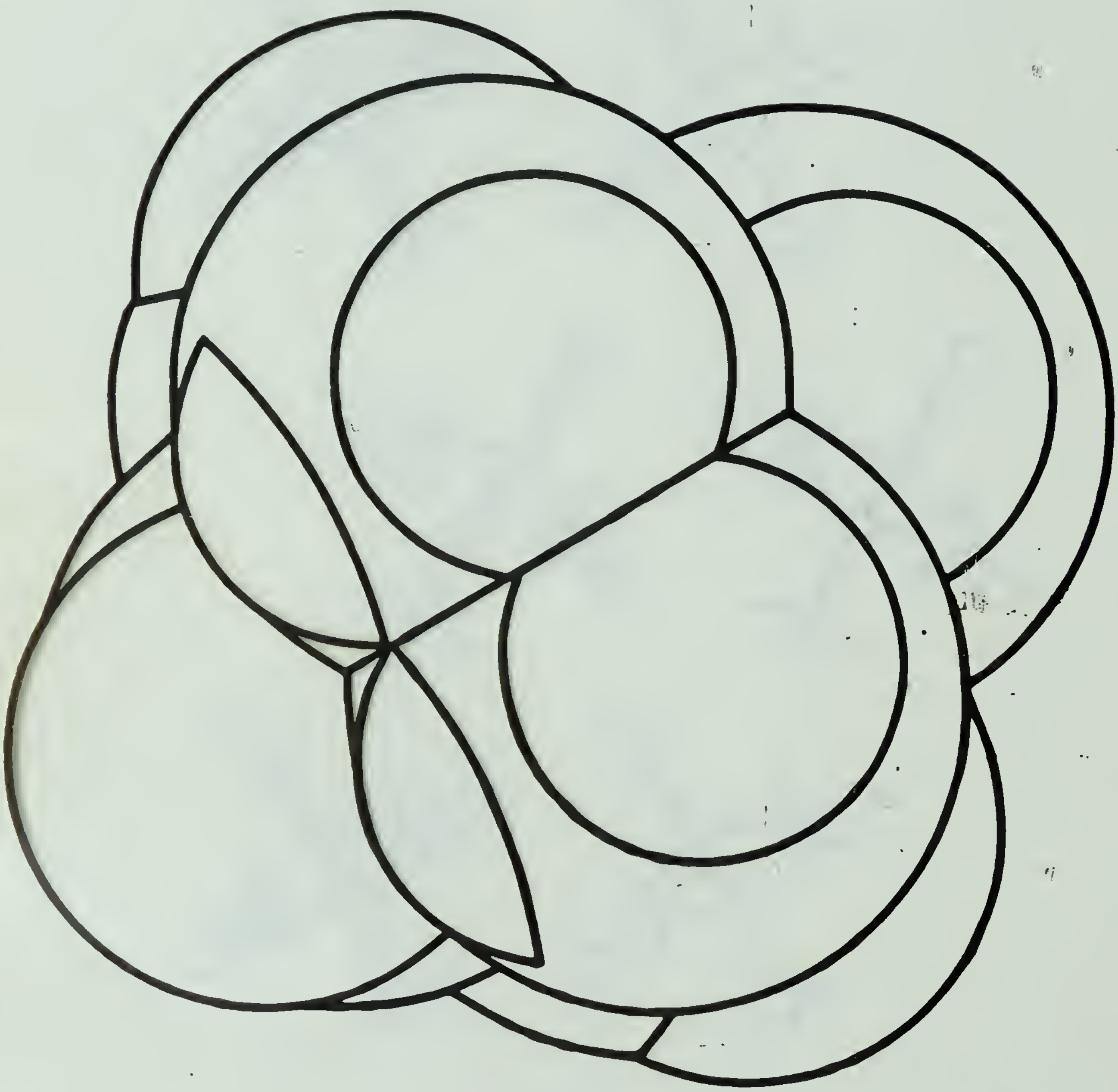


Figure(XVI)

Showing van der Waals radii in $(CO)_4Fe(Si(Me)_3)_2$

from the y direction

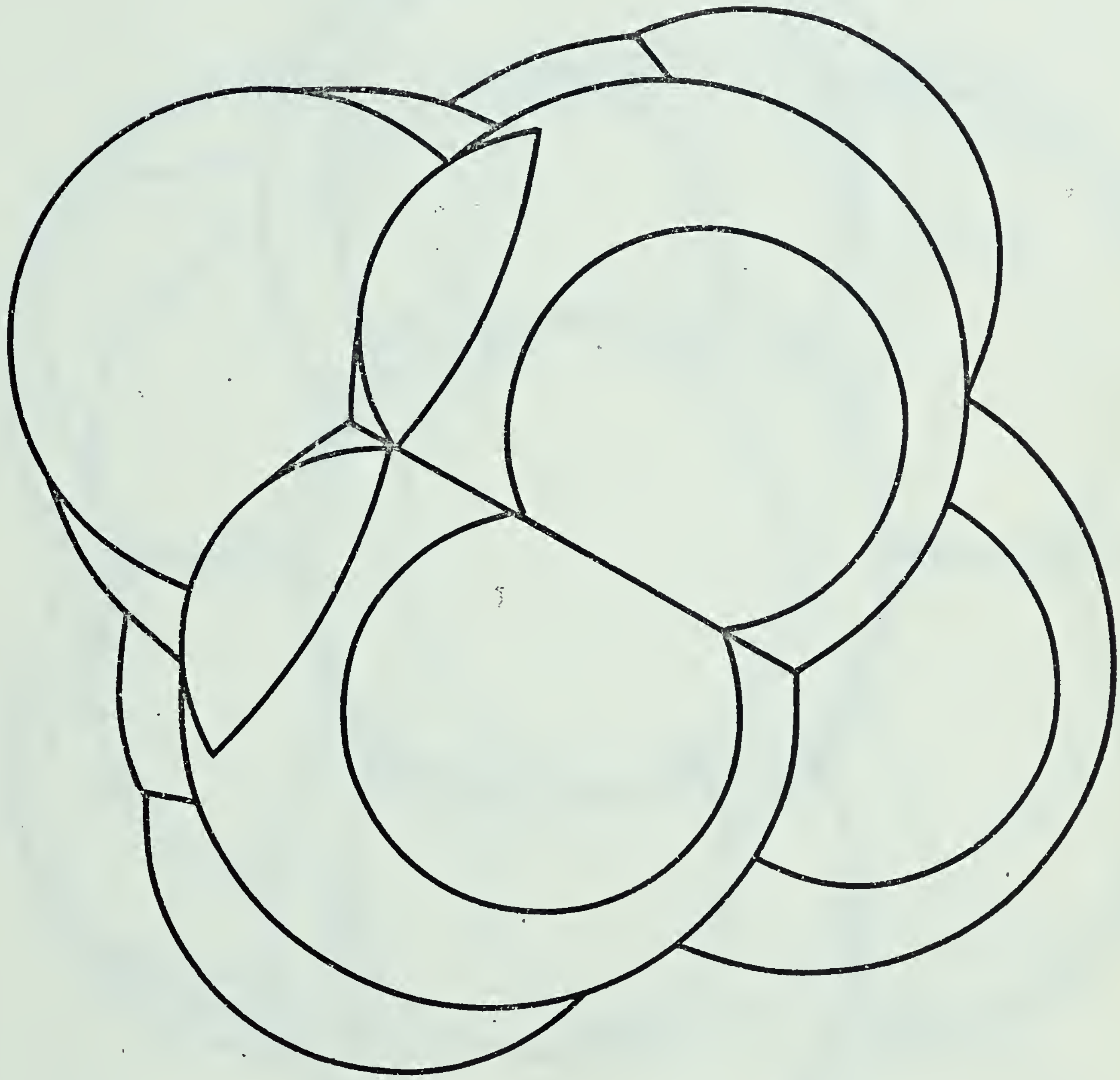




Figure(XVI)

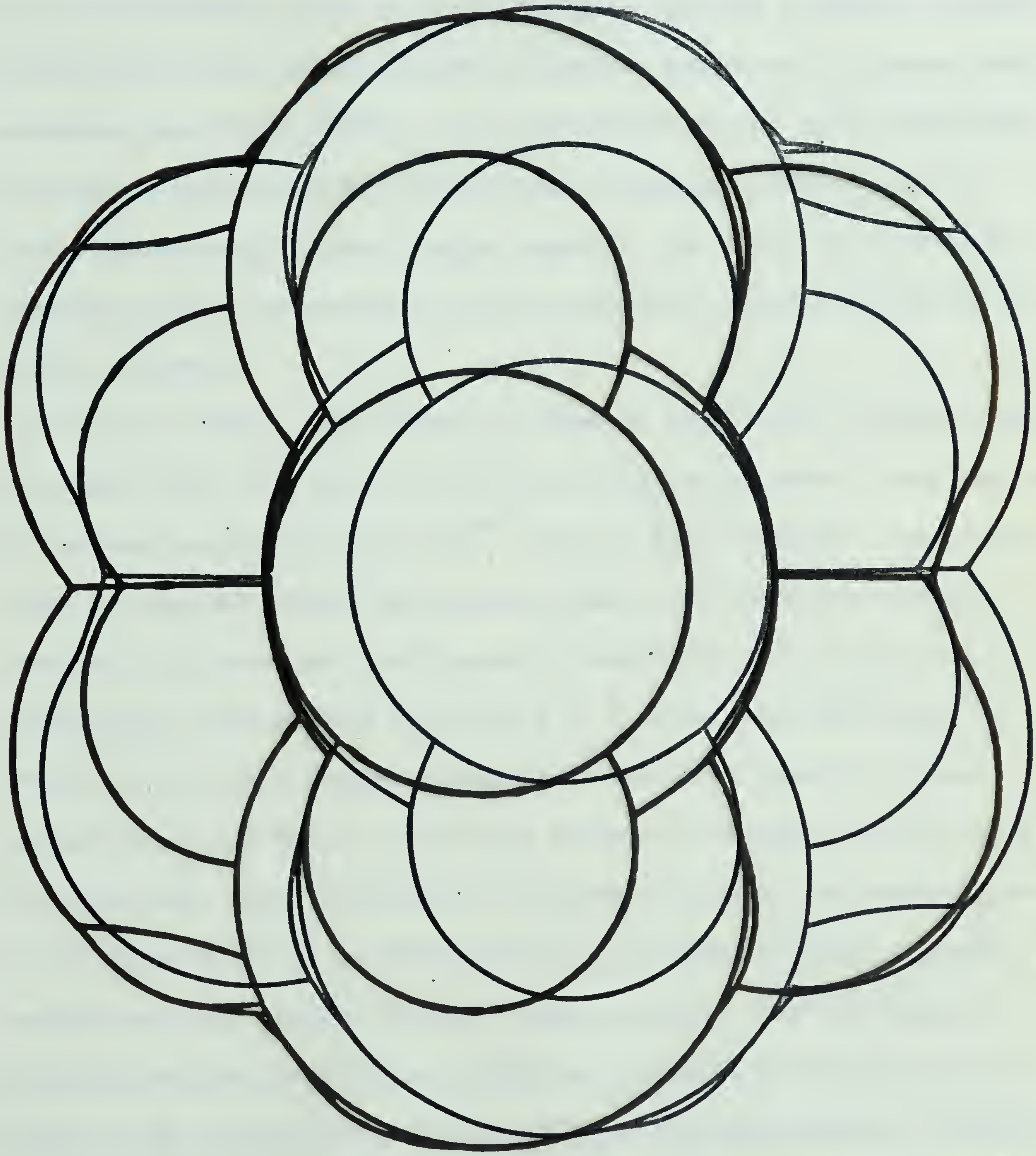
Showing van der Waals radii in $(CO)_4Fe(Si(Me)_3)_2$

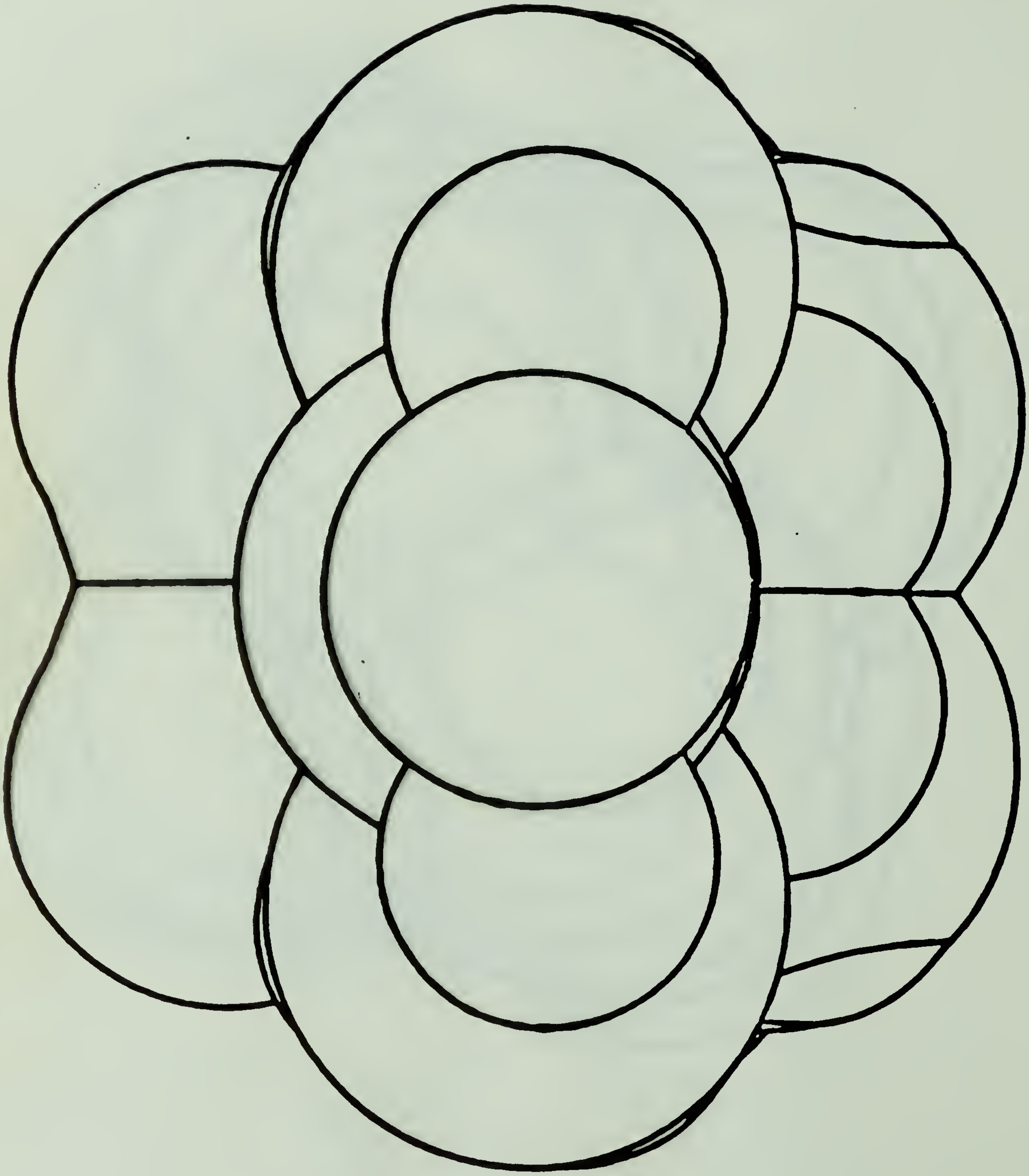
from the y direction



Figure(XVII)

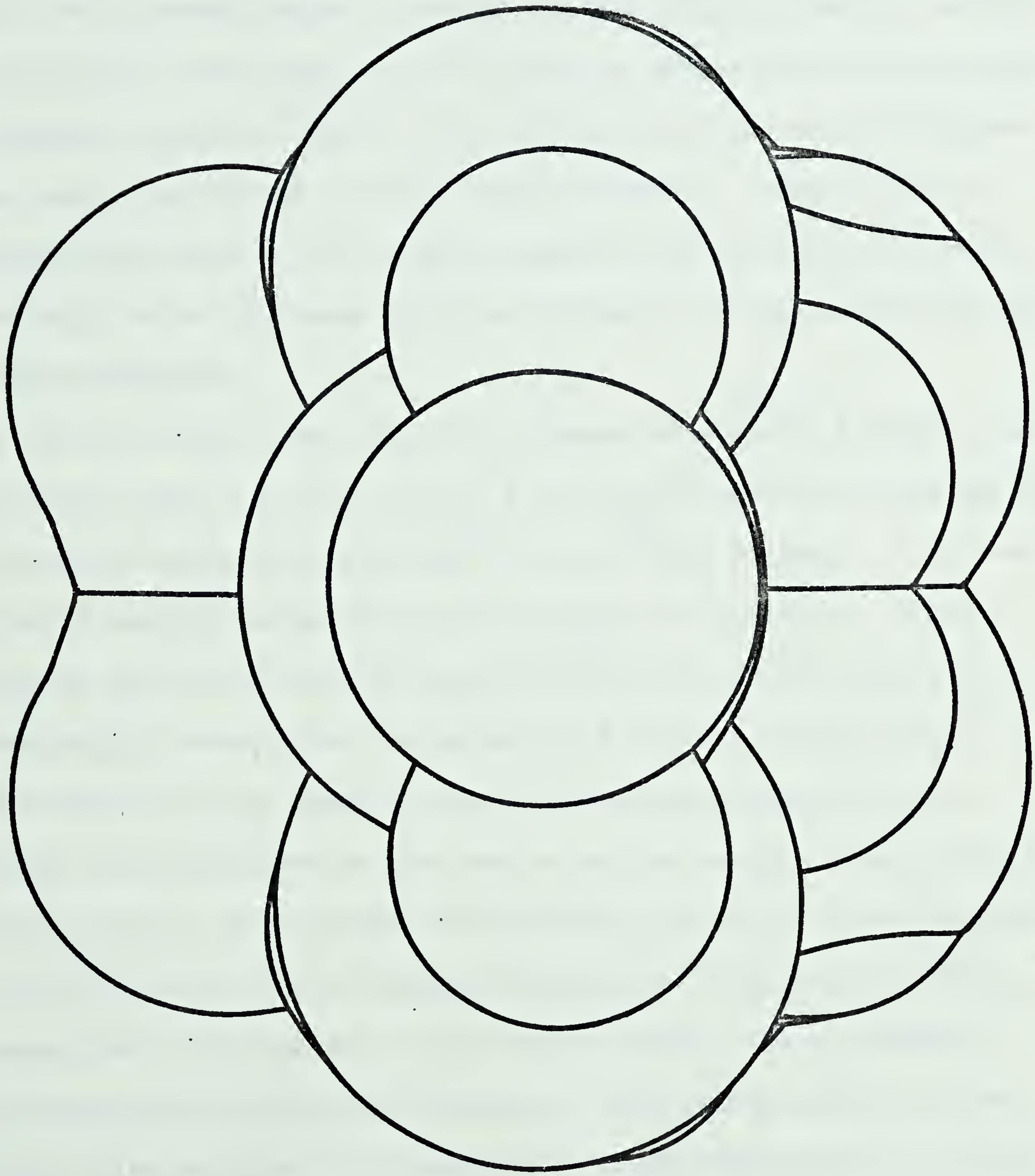
Showing a similar view from in the mirror plane y=1/4





Figure(XVII)

Showing a similar view from in the mirror plane y=1/4

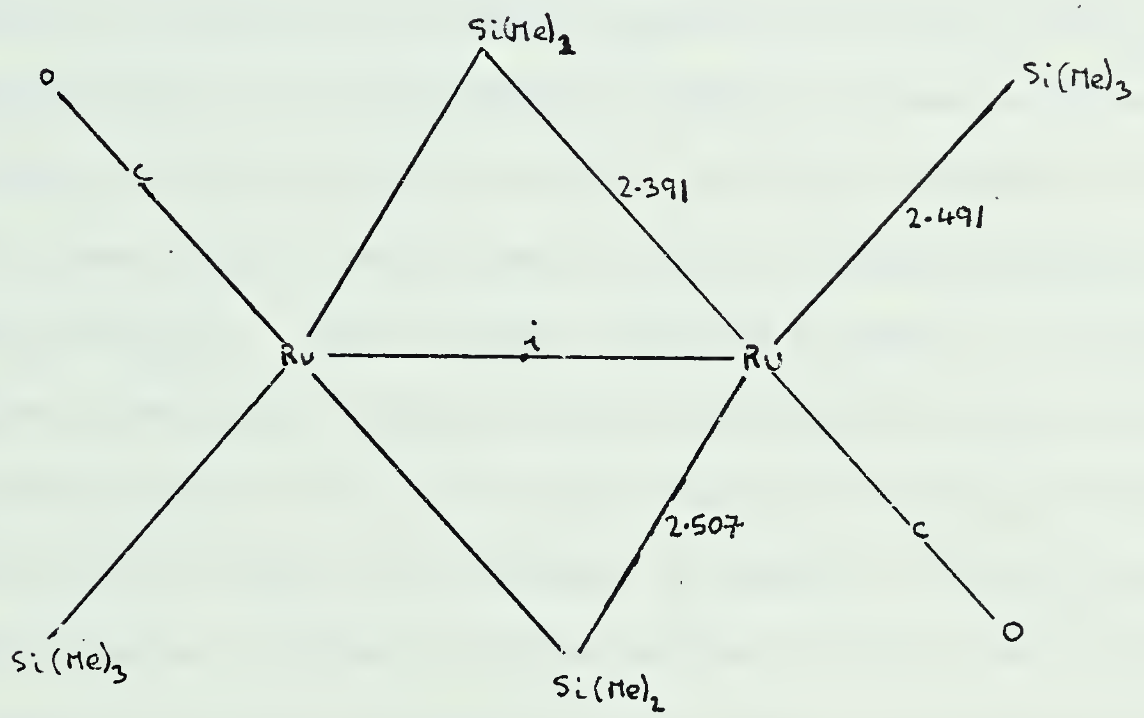


Any discussion of the molecular geometry must be prefaced by a caution concerning the effects of the disorder. Although the predominate and alternate images interpenetrate and produce a similar van der Waals surface, the atomic centres of the two images are in general well separated (see Table (XXVI)). The coordinates of the methyl hydrogens also may be influenced by the alternate component. However, the internal consistency of bond lengths suggests that the disorder does not seriously effect the geometry of the predominate molecule, although this might be expected.

The iron silicon bond length is observed at 2.455(2) Å which is surprisingly close to a value of 2.45 Å that can be estimated using the sum of covalent radii (1.34 for iron[96] and 1.11 Å for silicon). The latter value of covalent radius for silicon seems to be consistent with the observed silicon-carbon bond lengths in alkyl and aryl silanes and is considerably shorter than the value 1.17 Å which is normally used[45]. This latter value is based on silicon-silicon bond lengths in homonuclear bonds and known to give poor values for average covalent radii in many cases. This iron-silicon distance is longer than those observed (2.415 Å and 2.334 Å) in $Fe(CO)_4HSi(C_6H_5)_3$ and $Fe(CO)_4(SiCl_2)_2Fe(CO)_4$ respectively (references 43 and 97 respectively). The shortening of the metal-silicon bond in the latter two compounds is expected on the basis of the increased electronegativity of the substituents. The iron-silicon bond length of 2.456(2) Å can be compared with the ruthenium-silicon bond lengths observed in $Si(CH_3)_3(CO)_3Ru(Si(CH_3)_2)_2Ru(CO)_3Si(CH_3)_3$ (reference 98) shown in Figure (XVIII) overleaf.

Figure (XVIII)

A schematic diagram of a molecule containing three independent Ru-Si bonds.



One of the ruthenium-silicon distances is actually shorter than the iron-silicon distance while the other two ruthenium-silicon distances are only 0.05 Å longer. The difference in the covalent radii of iron and ruthenium can be estimated to be 0.16 Å from the difference of metal-carbon distances in ferrocene[99] and ruthenocene[100]. While the

coordination of ruthenium in the cluster compound is not identical with the coordination of iron in this compound it seems reasonable to suggest that the bond length data support the view that transition metal-silicon bonds are shorter (in a relative sense) when the metal is a second or third row transition series element.

The average of the three independent iron-carbon distances is 1.775 Å which can be compared with average values of 1.785 Å and 1.816 Å in $Fe(CO)_4HSi(C_6H_5)_3$ and $(CO)_4Fe(SiCl_2)_2Fe(CO)_4$ (references 43 and 97 respectively). The iron carbon bonds in the latter compound are significantly longer than the equivalent distances in $Fe(CO)_4(Si(CH_3)_3)_2$ and $Fe(CO)_4HSi(C_6H_5)_3$. This is simply explained in terms of the enhanced electron withdrawal by halosilyl groups (by comparison with alkyl and aryl silyl groups) and a concommitant reduction in π electron withdrawal by the carbonyl groups. The presence of disorder in $Fe(CO)_4(Si(CH_3)_3)_2$ makes it unwise to attempt to differentiate the iron carbon bonds and correlate iron carbon distances with the nature of the trans ligand. However, it should be noted that cis-$Fe(CO)_4X_2$ species show little evidence for significant variations within a given structure dependent upon the trans ligand (references 101 to 106 inclusive). Similar derivatives have been made for $Ru(CO)_4(GeCl_3)_2$ which has been studied in both cis and trans isomers[107]. These systems deny the straightforward deduction of trans influence as claimed for systems of the type $Cr(CO)_5L$ which is perhaps indicative of the subtlety of the cis and trans influences of ligands in octahedral π bonded compounds[108].

The trimethylsilyl ligands appear to have a perfectly normal geometry. The average silicon-carbon distance of 1.86 Å and average metal-

silicon-carbon angles of 112° should be compared with 1.88(3) Å and 114(1)° for the equivalent parameters in $Ru_2(CO)_6(Si(CH_3)_2)_2(Si(CH_3)_3)_2$ (reference no. 98). The orientation of the two trimethylsilyl groups with respect to each other is totally unexpected in that two methyl groups (C(7) and C(7')) point almost directly at one another. However, this contact at 3.437(7) Å would be considered attractive. The hydrogen-hydrogen contacts between these methyl groups correspond to repulsion[46] and the Si-Fe-Si' angle of 112° is consistent with net repulsion between the trimethylsilyl groups.

Large deviations from the angles of an idealised octahedral structure as exemplified by the Si-Fe-Si' angle are common in this structure. Only the C(1)-Fe-C(1') angle at 89.5° is within 1° of its idealised value. The sum of the angles Si-Fe-Si',C(1)-Fe-C(1'),Si-Fe-C(1) and Si'-Fe-C(1') is 359.9° indicating the coplanarity of the atoms Fe,Si,Si', C(1) and C(1'), which is perhaps better shown by the least squares plane calculation in Table (XXXI) below.

Table (XXXI)

Equation of Plane $0.5268x + 0.8500z + 0.5295 = 0$

Atom	Deviation from plane (Å)
Fe	0.004
Si	0.002
Si'	0.002
C(1)	-0.012
C(1')	-0.012

The angle Si-Fe-C(1) (and by symmetry the angle Si'-Fe-C(1')) is 79.3°. This angle which is smaller than the idealised value corresponds to the very favourable cis ligand interaction in that C(1) approaches the silicon atom so that it is equidistant from C(1), C(6) and C(7). This is the "bisecting" geometry associated with the close hydrogen-silicon contacts and in this case dictates the unusual arrangement of methyl groups centred on C(7) and C(7'). The remaining angle of interest, C(3)-Fe-C(4) is 141.3° and shows a massive distortion from the idealised value of 180°. The magnitude of this distortion is unprecedented in cis $Fe(CO_4X_2$ derivatives. Distortions to angles of 156° and 165° have been claimed for the two independent molecules in the structure of $((CO)_4FeSn(CH_3)_2)_2$ (reference no. 106), but the reliability of this data is low due to severe disorder problems. Distortions of these trans C-Fe-C angles would normally be less than 10° (references 101 - 105 inclusive). In the present structure the distortion relieves the intramolecular repulsions C(4)-C(6) and C(3)-C(5).

The magnitude and sense of the distortion in cis-$Fe(CO)_4(Si(CH_3)_3)_2$ leads to an interesting description of the structure. The four carbonyls can be considered to form a distorted tetrahedron and the silicon atoms can be treated as occupying the centres of faces of the tetrahedron. While the description may seem artificial it is particularly pertinent when discussing possible modes of stereochemical non-rigidity in octahedral complexes especially in the light of structural and spectroscopic studies of the system $H_2Fe(P(OC_2H_5)_3)_4$ by Muetterties et al.[109,110]. Muetterties introduced a new possible mechanism of polytopal rearrangement for the hydride systems. Therefore mechanisms which have been pro-

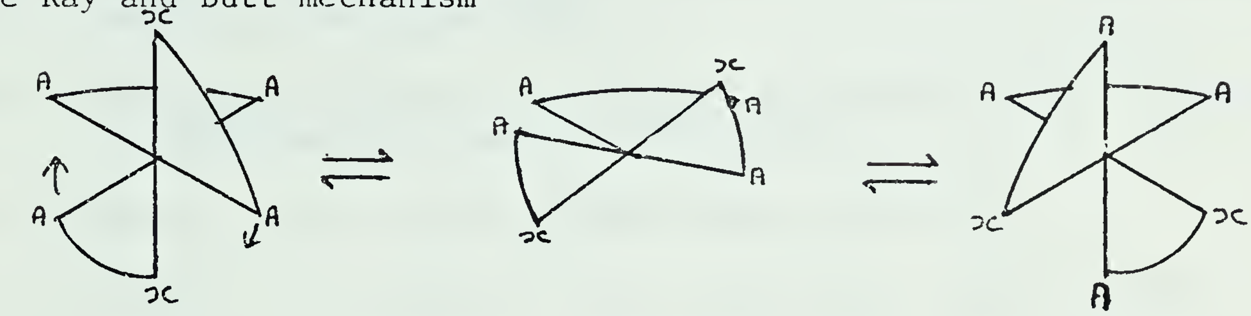
posed for non-dissociative rearrangement of octahedral complexes are shown overleaf in Figure (XVIII). The first three mechanisms all involve interconversion of cis and trans isomers. The Muetterties mechanism which involves hydrides tunnelling through edges of a tetrahedral array of phosphorus atoms leads to interconversion of cis and trans isomers and allows permutation of the phosphite ligands. However, it has a transition state when both hydrogen atoms are simultaneously at an edge and this species corresponds to a highly distorted 'trans' isomer which could have a significant lifetime.

The particular distortions observed for cis-$Fe(CO)_4(Si(CH_3)_3)_2$ suggest that the Muetterties mechanism which was proposed for hydridic species may well be relevant for much heavier groups. The quasi tetrahedral arrangement of carbonyl groups in the solid state structure does not prove that the mechanism of stereochemical non-rigidity is that of Muetterties, but it does indicate that Muetterties type transition states may be accessible.

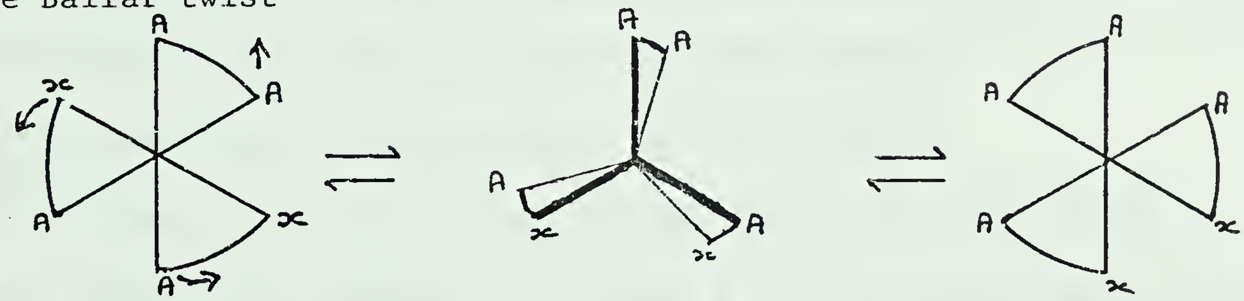
Figure(XIX)

Non-dissociative mechanisms for the rearrangement of octahedral complexes.

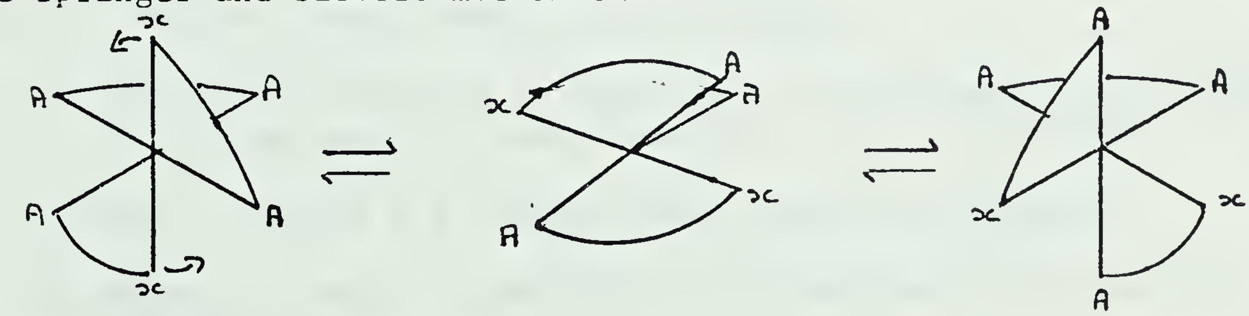
The Ray and Dutt mechanism[111]



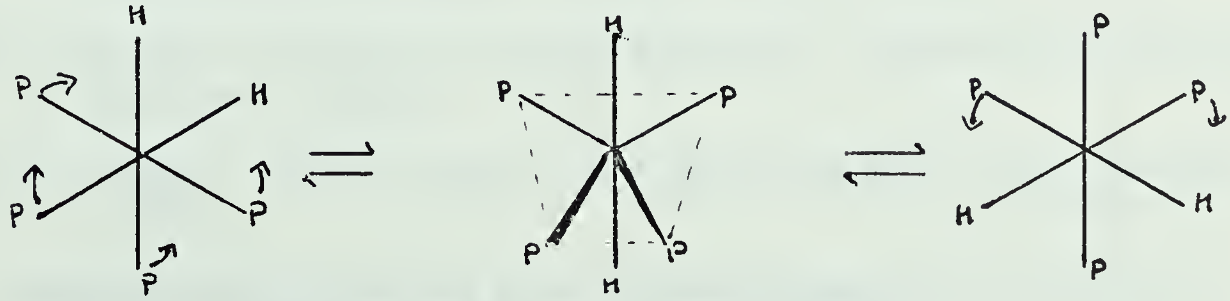
The Bailar twist[112]



The Springer and Sievers mechanism[113]



The Muetterties mechanism[109,110]



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Appendix I

Programmes used in Crystal Structure Solution, refinement and analysis.

Author	Programme	Description
D.P. Shoemaker	MIXG2	Calculates picker diffractometer settings from unit cell dimensions and type.
M.J. Bennett	PMMO	Transforms raw data to intensities applying Lp corrections.
M. Elder and K.A. Simpson	D-REFINE	Refines cell parameters for all space groups, used on the manual instrument.
W.R. Busing and H.A. Levy	FACS CELL DIMENSIONS	Refines cell parameters for all space groups, used on the FACS automated instrument.
A. Zalkin	FORDAP	Fourier summation for Patterson or Fourier maps.
W.C. Hamilton	GONO9	Absorption corrections for Picker Data
P. Coppens	DATAB	Absorption and extinction corrections.
C.T. Prewitt	SFLS5	Structure factor calculations and least squares refinement of parameters, modified by B.M. Foxman and M.J. Bennett for rigid body routine, and by M.J. Bennett and W.L. Hutcheon for the hindered rotor.
J.S. Woods	MGEOM	Calculates bond lengths, angles and best planes.
W. Busing and H.A. Levy	ORFFE	Calculates bond lengths, angles and associated standard deviations modified by B. Penfold for I.B.M. 360 and W.L. Brooks & M. Elder for hindered rotors and rigid bodies.
C. Johnson	ORTEP	Writes Plot Command for Calcomp plotter, for plotting three dimensional molecular representations

Author	Programme	Description
M.J. Bennett and B.M. Foxman	MMMR	Calculates starting parameters for rigid bodies and hindered rotors.
M. Cowie	PUBE	Sorts data according to any desired sequence of h, k and l.
R.C. Elder	PUBTAB	Prints Structure Factor Amplitude tables; modified by M. Cowie to work in conjunction with PUBE.
G.J.B. Williams	FRAME	Converts continuous paper tape output from automatic diffractometer, in ASCII code to "framed" output on cards in EBCDIC coding, suitable for PMMO input.

A list of crystallographic definitions used in this work, but not applicable to all diffractometers on data collection methods.

Symbol	Name	Description
L	Lorentz Factor $L = \dfrac{1}{\mathrm{Sin}\theta_{hkl}}$	A factor which corrects for the varying rate with which reflections pass through the sphere of reflection during a scan.
P	Polarisation Correction	A polarisation correction allowing for the effects of the polarisation of an X-ray upon Bragg reflection.

$$p = (\cos^2(2\theta_{monochromator}) + \cos^2(2\theta_{hkl})$$

R_1	Residual or Reliability Index $R_1 = \dfrac{\Sigma(\lvert\lvert Fo\rvert - \lvert Fc\rvert\rvert)}{\Sigma\lvert Fo\rvert}$	Measure of the goodness of the fit of the model to the observed intensities, but some other authors use different definitions of an "R" factor.
	Residual or Reliability Index $R_2 = \left(\dfrac{\Sigma\omega((\lvert Fo\rvert - \lvert Fc\rvert)^2)}{\Sigma\omega(\lvert Fo\rvert^2)}\right)^{1/2}$	

Diffractometers used for data collection and settings used.

Two diffractometers were used in data collection, both were Picker Four Circle Diffractometers. The data sets for the first and last substances whose crystal and molecular structure are reported in this thesis were collected on a manual instrument and the data sets for the other three compounds were collected on an instrument automated by the FACS system.

A graphite monochromator (002 reflection) was used with both copper and molybdenum radiations in order to give a monochromatic beam, free of k_β radiation, and with reduced white radiation.

The intensities of the diffracted beam were measured on a scintillation counter in conjunction with a pulse height analyser, tuned to accept 95% of the K_α peak. Measured intensities which were in excess of 10^4 counts/sec overwhelmed the counter and these reflections were therefore recollected with a less intense beam and appropriately scaled to merge with the remaining data.

The target-crystal distance was 20 cm, the crystal-counter distance was set at 20 cm. A variety of collimator radii were employed, depending on the size of the crystal under investigation.

Appendix (II)

Introduction

Hückel's 4n + 2 rule implies the possibility of an aromatic 10 membered ring. Elegant work by Vogel[114] et. al. lent support to the validity of this rule, but 1,6-Methano [10] annulene is not planar[115], and therefore, not rigourously demonstrative of the properties of the planar 10 π-system. A regular planar 10 sided figure would have C-C-C angles of 144^{o}, a severe distortion from the "ideal" 120^{o}. Ring systems with two carbon-carbon triple bonds would, however, be expected to contain four 180^{o} angles and six 120^{o} angles and compounds of this kind should be especially suited for the investigation of planar 10-π electron systems[116].

Recently a novel attempt to prepare a new 10-π electron aromatic hydrocarbon was described[117]. The final step of the reaction scheme produced 1,2,3,4 tetrahydroanthracene and, in 30% yield a new hydrocarbon with molecular formula $C_{14}H_{12}$. The spectroscopic properties of the compound were consistent with two possible structures I(a), containing the desired 10 electron system, and I(b) a rearrangement product shown in Figure (XX) overleaf.

[illegible]

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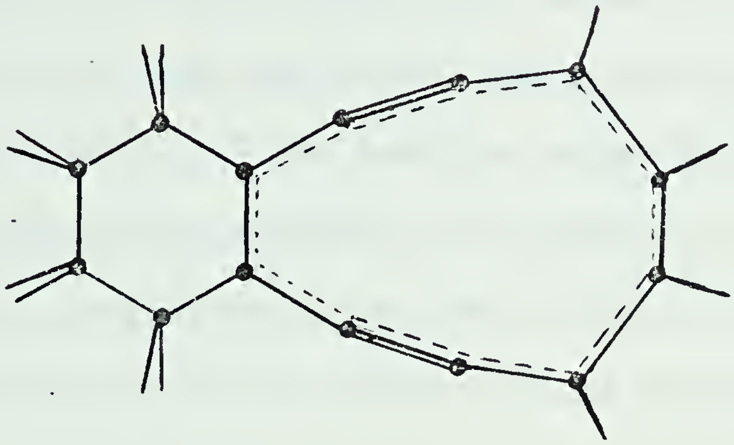
[illegible]

[illegible]

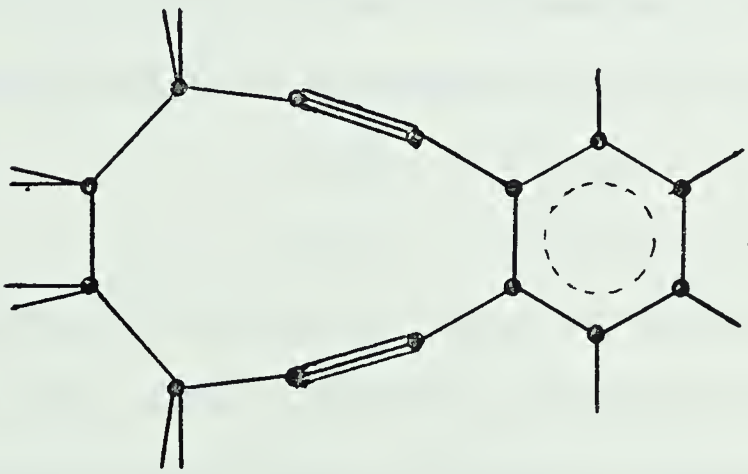
Figure (XX)

The two possible molecules, under consideration, and having the formula

$C_{14}H_{12}$



I(a)



I(b)

The X-ray diffraction study was undertaken to resolve the question of gross stereochemistry and, to provide precise bond lengths for the new aromatic species, if the structure was found to be I(a).

Experimental

Colourless tetragonal bipyramidal crystals of the substance were kindly supplied by Dr. S. Masamune. Investigation showed the crystals to be unstable in air and samples were sealed in Lindemann glass capilliaries with a nitrogen atmosphere. The crystals supplied had crystal faces of the form {1,1,3} but were too large for diffraction studies and repeated attempts to grow smaller ones failed. The crystal did not cleave cleanly, but shattered to give irregular fragments, however, some fragments were found to be suitable in size and shape for a diffraction study.

X-ray photographs taken with a Weissenberg Camera led to the assignment of the crystal glass as tetragonal and the diffraction conditions

$$0\ 0\ \ell \qquad \ell = 4n$$

$$h\ 0\ 0 \qquad h = 2n$$

are consistent with space group $P4_12_12$ (no. 92) or the enantiomorphous $P4_32_12$ (no. 96). Since the anomalous dispersion effects are too small to distinguish between these an arbitrary assignment of the latter was made for the study of the crystal. A fresh crystal of external dimensions 0.025 x 0.02 x 0.025 cm was mounted with the a axis parallel to the goniometer head axis. A least squares refinement of 2θ values for 13 reflections, which were carefully centred on a Picker Four Circle manual diffractometer (using CuK_{α_1} radiation, λ = 1.54051 Å, and no monochromator) gave precise lattice parameters a = 7.891(1) Å, c = 17.108(1) Å at 27°C with standard deviations given in brackets. The standard deviations of the unit cell dimensions provide an overoptimis-

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

tic estimate of the true errors. Consideration of likely errors in temperature (approximately $2^{o}C$) and typical coefficients of linear expansion for molecular crystals (approximately 10^{-4}) would lead to more realistic estimates of the cell dimensions and their errors as a = 7.891(3), c = 17.108(5) Å.

The observed density, 1.12 g/cm^3 was in good agreement with the calculated value of 1.12 g/cm^3, based on four formula weights per unit cell, and required the molecules to possess an internal 2-fold axis of rotation. The very good agreement between the observed and calculated densities is probably somewhat fortuitous as the density was measured by flotation in potassium iodide solution and the crystals decomposed in less than ten minutes under these conditions. The X-ray diffraction patterns show a rapid decrease in observable intensities with $\sin\theta/\lambda$. This behaviour is typical of poorly ordered crystals and indicates that the structural determination would yield results of low precission. The non-centrosymmetric space group decreases the number of independent observations that can be made[16]. Despite the poor prognosis, the room temperature structure determination was pursued to provide immediate information on the gross stereochemistry of the molecule.

The data were collected using CuK_{α} radiation and the intensities of 519 independent reflections, limited by $0 < 2\theta < 120^{o}$, were measured in all. A graphite monochromator (002 plane) was used in conjunction with a take off angle of 3^{o}. One minute scans through 2^{o} were employed in the intensity measurement, the area under the peak being integrated. The background on either side of the peaks, B1 and B2, was measured for 20 seconds in the stationary positions. Making the assumption that the

background was a linear function in 2θ the data were reduced to structure amplitudes ($|F|$) and their standard deviations (σF) following the procedure of Doedens and Ibers[22]. A value of $p = 0.03$ was used to calculate σF where p is a term not related to pure counting statistics. The intensities of 250 reflections were found to be significant using the criterion $I/\sigma I > 3$. These 250 reflections were used in further calculations.

Six standard reflections were measured every three hours to monitor crystal decomposition and to check on crystal alignment. No significant decrease in the intensities of the standards were observed during data collection. No absorption corrections were applied as the linear absorption coefficient (μ) was only 5 cm^{-1} for CuK_{α} radiation and variations in the transmission factors would be less than 5% for the study crystal.

Solution and Refinement of the Structure

The structure was solved by trial and error methods. The reflections 004 and 113 had very large structure amplitudes and whilst that of 004 was larger it was quadrupally weighted. Since the molecule, regardless of whether it adopts structure I(a) or I(b) was thought to be approximately planar, and required by symmetry considerations to sit along the two-fold axis the unusual magnitude of the 113 reflection was consistent with a coincidence of one of the molecular planes with the crystal 113 plane. Since only faces of the form {113} are developed on the crystals the habit added weight to this consideration. These initial deductions suggested a model with the molecules bisected by the two-fold axis with

the molecular planes inclined at about 45° to the two-fold axis. Structure factor calculations for the 004 reflection were also consistent with this angular orientation.

The models under serious consideration have very similar shape as estimated by molecular models and are approximately planar with only 2 out of the 14 carbon atoms in the structure likely to show any large deviation from the mean molecular plane. Five models of varying shape for the ten-membered ring were constructed and placed on graph paper and the fractional coordinates found in an arbitrary position along the diagonal.

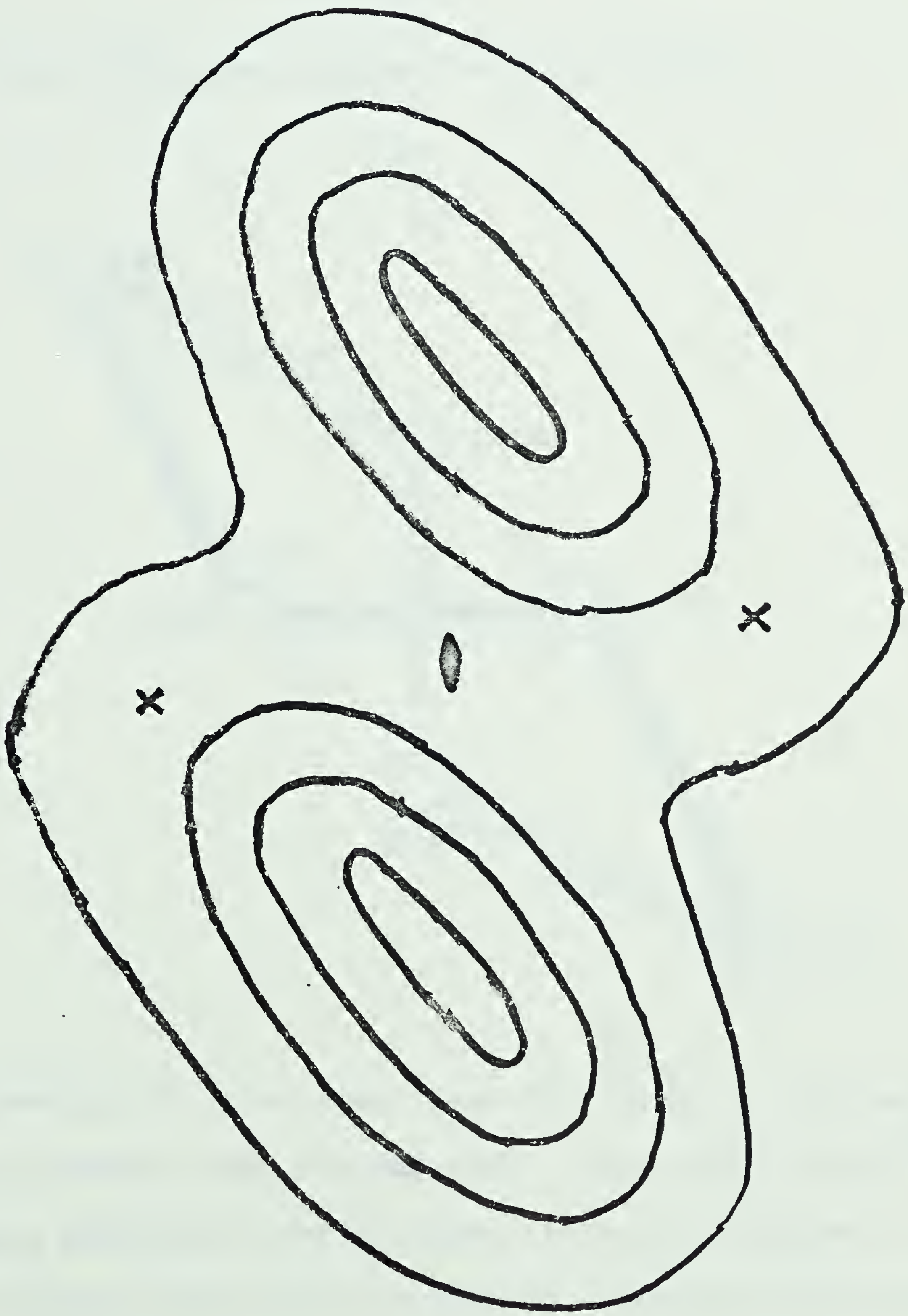
A short programme which was devised to treat this particular problem is given in Appendix (III). The structure amplitudes of a limited number of reflections and associated R values were calculated on the basis of the input model. Structure factors for the carbon atoms were obtained from the International Tables[19]. The fractional coordinates in x and y were then increased by 0.01 and the calculations repeated until the model had travelled half the length of the diagonal. On reaching this point the model was returned to the starting position, tilted through 5° with respect to the c axis and the calculations repeated as outlined above. One of these models gave rise to a clearly defined minimum with a tilt of 50° with respect to the c axis. Examination of the structure factor expressions showed that reflection with ℓ odd were affected in both sign and magnitude by the sense of the tilt, whereas those with ℓ even were unaffected. Two structure amplitude calculations on the full data set were made, one with each of the two senses of tilt. One model was much better than the other giving 40% and 50% for R1 and R2 respec-

tively as opposed to 50% and 60% for R1 and R2 for the poorer model. The model giving the better fit was then subjected to least squares refinement procedures, the function being minimised was $=\Sigma\omega(|F_o|-|F_c|)^2$

Eleven cycles of least squares refinement with all atoms isotropic reduced R1 to a constant 13% and an examination of the bond angles and distances of the refined model showed I(b) to be correct. The positions of the hydrogen atoms were then calculated assuming a C-H distance of 1 Å and the usual ideal geometry for the carbon atom hybridisation schemes sp^2 and sp^3. The inclusion of these hydrogen atoms in structure amplitude calculations reduced R1 to 12%. At this stage of refinement most bond lengths were in reasonable agreement with expected values[24], but two bond lengths C(1)-C(1') (1.40 Å) and C(1)-C(2) (1.67 Å) deviated considerably from their expected value of approximately 1.54 Å. The thermal parameters of both independent atoms C(1) and C(2) were unreasonably large and in an attempt to find out why five more cycles of least squares refinement with all atoms anisotropic were calculated, reducing R1 to 10%. The large thermal amplitude of atoms C(1) in the z direction indicated the need for further investigation. Electron density maps, that contained atoms C(1) and C(1') in the same section, were calculated. This objective was achieved by using the C centred tetragonal cell as the working cell instead of the standard primitive cell. A contour of the section containing atoms C(1) and C(1') indicated a disorder problem and the pertinent section of the electron density map is shown in Figure (XXI) overleaf.

Figure(XXI)

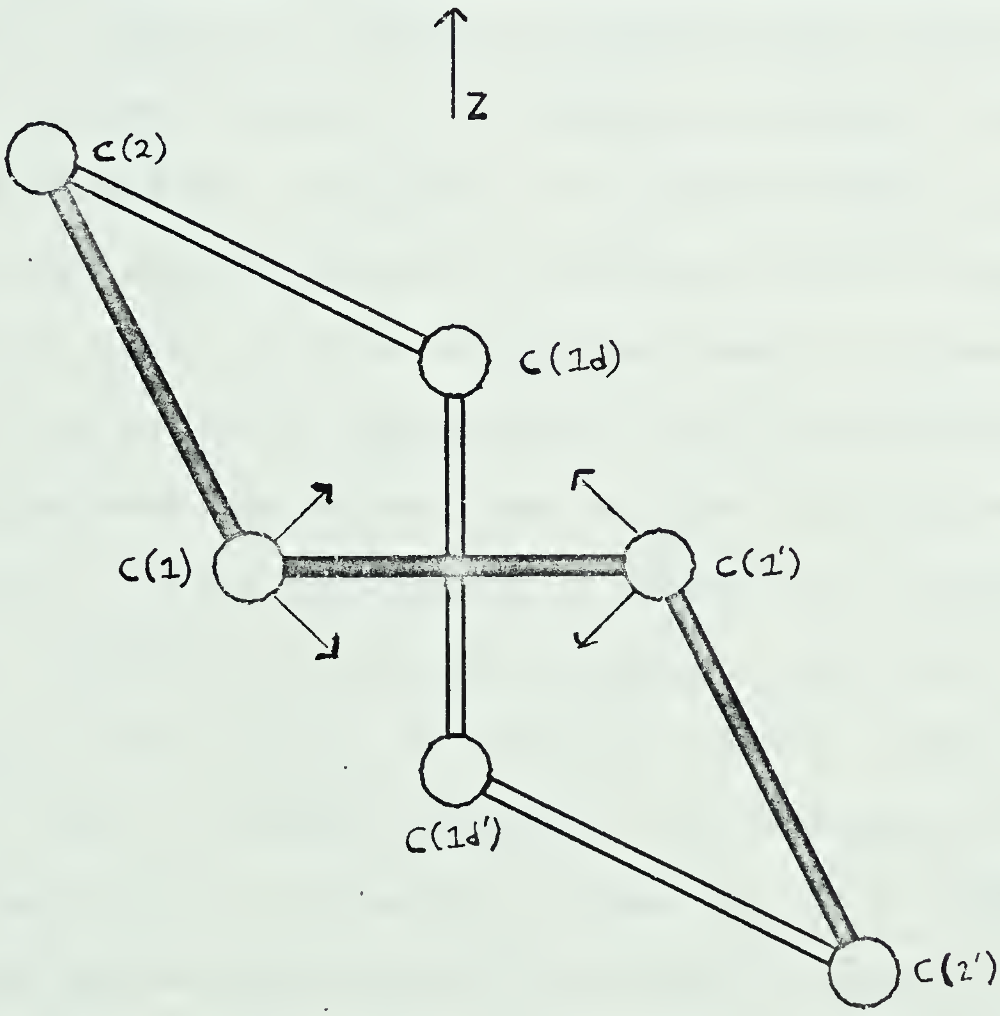
An electron density contour of the plane containing both symmetry related carbon atoms C(1) and C(1')



The nature of the disorder arises from the conformation of the atom sequence C(2)-C(1)-C(1')-C(2'), approximately 25% of the molecules have the opposite conformation as in Figure (XXII) below.

Figure (XXII)

A figure showing the disorder involving atom C(1).



Approximately 25% of the carbon atoms C(1) adopt the conformation shown by the unshaded atoms labelled C(1d). Since C(1d) and C(1d') are approximately equidistant from C(1) then C(1) would be expected to shift along the C(1)-C(1') bond vector, accounting for anomalous bond lengths involving atom C(1).

The unusual thermal parameters involving atoms C(1) and C(1') can then also be explained by the attempts of the undisordered model to spread the electron density into the region occupied by the atoms C(1d) and C(1d'). The arrows in Figure (XXII) indicate the shifts experienced by atom C1 accounting for the increase in the C(1)-C(2) bond length and the shortening of the C(1)-C(1') bond length. Lack of data and parameter correlations make it difficult to refine the disorder model using the least squares programme directly. The disorder was assumed to involve only atoms C(1) and C(1') and, subsequently, the associated hydrogen atoms. Clearly C(2) and C(2') might be expected to be affected, but the more reasonable temperature factors of C2 in the previous stages of refinement suggested that any deviations were small and would be impossible to resolve. The disordered atom C1d was fixed such that the distances C(2)-C(1d) and C(1)-C(1d) were 1.54 Å and the mid-point of C(1d)-C(1d') was coincident with the mid-point of C(1)-C(1d). The atoms C(1) and C(1d) were constrained to have fixed occupancy factors and only the temperature factors of C(1) and C(1d) were allowed to vary. Isotropic refinement of the structure was then attempted using 10, 20, 25, 30 and 40% occupancy for the atom C(1d). After each refinement C(1d) was shifted manually such that the geometrical restraints outlined above held. Table (XXXII) overleaf lists some of the resulting values.

Table (XXXII)

A comparison of various occupancy values for the disorder in $C_{14}H_{12}$.

% occupancy for C(1d)	10	20	25	30	40
R1	13.4	10.9	10.7	10.8	11.7
R2	16.8	13.8	13.7	13.8	15.1
B for C(1)	9.21	8.78	7.20	7.48	5.99
B for C(1d)	-7.76	4.79	6.30	8.83	10.50

The 25% occupancy model was taken to be most likely and may be justified using Hamilton's statistical test of residuals[52]. Hydrogen atom positions were re-calculated and were included in subsequent structure factor calculations. The hydrogen atoms which were attached to C(1) were labelled H1(1) and H1(2), those attached to C(1d) were labelled H1d(1) and H1d(2) and the 25% and 75% occupied hydrogens on C2 were labelled H2d(1)-H2d(2) and H2(1)-H2(2) respectively. The hydrogens attached to C(6) and C(7) were labelled H(6) and H(7) respectively. Thermal parameters for these hydrogens were set at 10% greater than the carbon atoms to which they were attached, but their parameters were not refined. Refinement of anisotropical thermal parameters for the carbon atoms was considered unwise in view of the paucity of data and the model was constrained to isotropic thermal parameters in the final stages of refinement. Three cycles of least squares refinement then reduced R1 to 8.6% and R2 to 10.4%. Refinement was considered complete when the max-

imum shift/standard deviation of the parameter was less than 0.1 for all parameters varied. The final coordinates are listed in Table (XXXIII) overleaf and the final observed and calculated structure amplitudes in Table (XXXIV), after Table (XXXIII).

Table (XXXIII)

Carbon Atom Parameters

Fractional Coordinates x 10^4

Atom	x	y	z	U
C(1d)	1174	915	-442	0.053
C(1)	1674(15)	230(17)	-33(9)	0.080
C(2)	2953(15)	317(15)	-665(6)	0.081
C(3)	4079(13)	1811(13)	-601(5)	0.074
C(4)	4902(12)	3018(13)	-498(5)	0.075
C(5)	5578(11)	4609(11)	-267(4)	0.065
C(6)	7143(13)	5229(13)	-516(5)	0.084
C(7)	7708(13)	6812(13)	-262(6)	0.098

Hydrogen Atom Parameters

Fractional Coordinates x 10^4

H1d(1)	290	10	-630	0.120
H1d(2)	930	2070	-720	0.120
H2d(1)	3380	-670	-330	0.120
H2d(2)	2950	-110	-1270	0.120
H1(1)	2390	460	560	0.104
H1(2)	1120	940	60	0.104
H2(1)	3699	-790	-700	0.104
H2(2)	2260	400	-1210	0.104
H(6)	7880	4450	-870	0.087
H(7)	8830	7270	500	0.111

Table (XXXIV)

Structure Amplitudes (x10)

A comparison of Observed and Calculated Structure Amplitudes (x10)

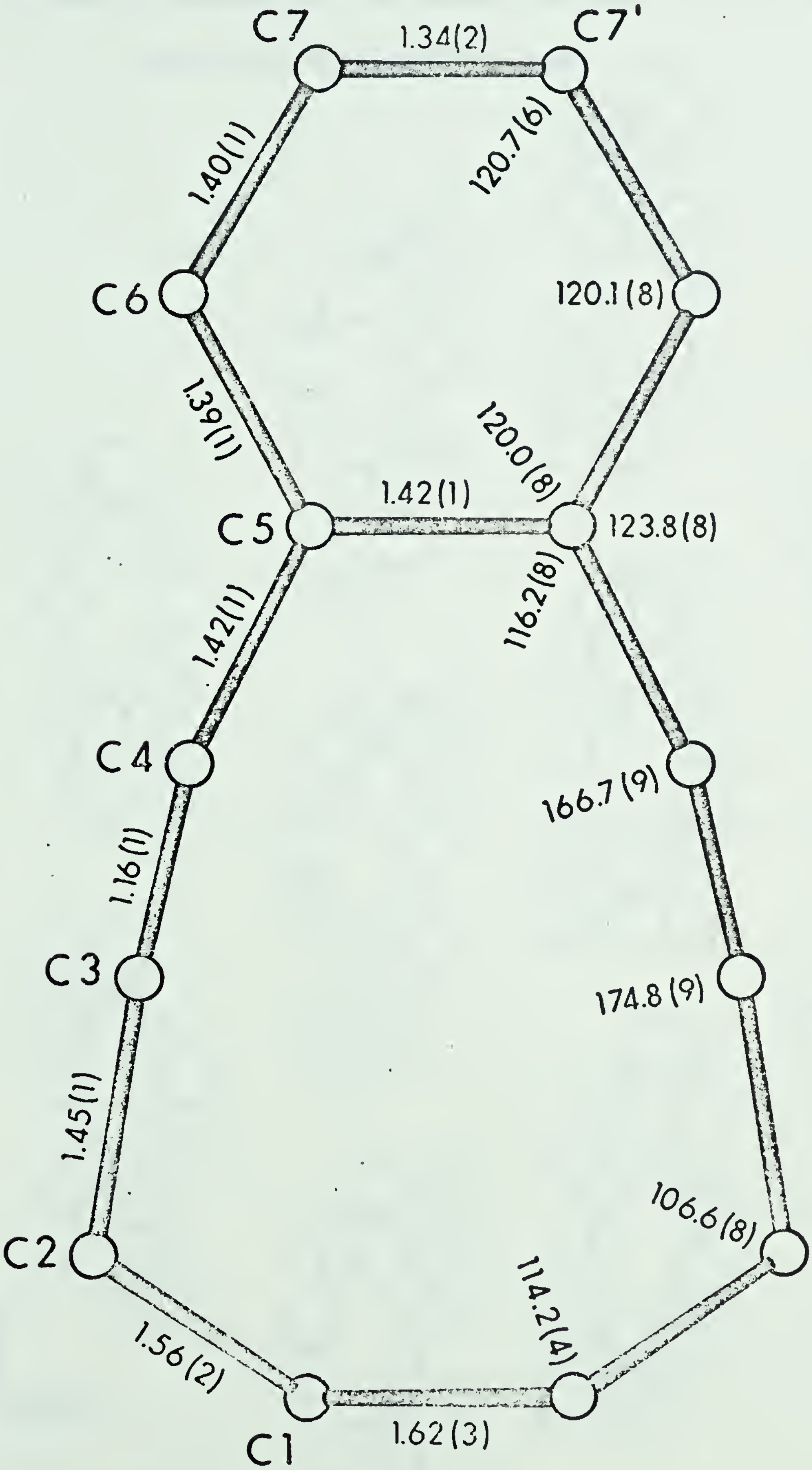
Table (XXXIV) contains only one page.

H	L	FOBS	FCAL
K = 0**			
0	4	539	1030
0	8	488	482
0	12	184	153
1	1	143	149
1	2	405	422
1	3	186	180
1	4	309	305
1	5	370	363
1	6	63	56
1	8	52	48
1	9	161	156
1	10	197	189
1	12	107	102
1	13	65	54
1	14	82	85
1	15	43	37
1	17	51	51
2	0	116	107
2	1	276	260
2	2	169	165
2	3	39	42
2	4	82	73
2	5	258	269
2	7	64	58
2	9	30	16
2	11	81	72
2	13	45	43
3	1	215	222
3	2	92	96
3	5	133	131
3	6	74	67
3	7	61	56
3	8	61	52
3	9	32	43
3	10	31	19
3	11	46	44
3	12	51	40
3	13	64	60
3	15	48	40
4	0	324	323
4	4	107	94
4	5	40	50
4	7	44	30
4	8	51	62
4	9	66	63
4	11	89	67
4	12	40	40
4	13	74	70
4	15	39	38
5	2	71	87
5	5	56	65
5	6	33	26
5	7	33	46
5	8	51	58
5	9	42	46
5	10	60	80
5	11	69	60
5	12	52	44
6	1	42	30
6	2	60	67
6	6	79	80
6	9	40	39
6	11	31	26
7	2	39	46
7	3	61	51
8	2	30	18
K = 1**			
1	0	466	517
1	1	87	80
1	2	559	593
1	3	862	909
1	4	403	411
1	5	525	535
1	7	313	300
1	8	110	109
1	9	37	22
1	10	93	94
1	11	33	32
1	12	57	50
1	13	87	95
1	16	41	35
2	1	266	264
2	2	126	123
2	3	427	418
2	4	38	32
2	5	104	116
2	6	75	76
2	7	285	274
2	8	50	46
2	9	73	70
2	10	111	102
2	12	41	43
2	14	35	38
2	15	34	23
2	18	33	33
3	0	166	167
3	1	53	54
3	2	43	43
3	3	105	99
3	4	55	43
3	5	101	100
3	6	114	110
3	9	52	51
3	11	45	35
3	13	75	68
4	0	53	43
4	2	177	176
4	3	48	44
4	4	46	54
4	5	52	48
4	6	43	54
4	7	30	40
4	8	51	54
4	9	66	72
4	10	45	54
4	11	50	37
4	13	41	36
4	15	40	31
5	0	43	52
5	1	49	53
5	2	48	47
5	3	97	106
5	4	32	42
5	5	63	81
5	6	53	27
5	7	36	38
5	8	49	31
5	9	79	75
5	10	33	30
5	11	31	21
5	12	36	27
5	13	38	33
6	0	40	29
6	3	44	48
6	4	46	47
6	6	50	53
6	7	70	77
7	4	51	52
7	7	44	45
K = 2**			
2	0	506	507
2	1	67	68
2	2	147	147
2	3	268	256
2	4	76	78
2	5	189	210
2	6	26	36
2	7	224	226
2	8	273	265
2	9	90	100
2	10	38	36
2	11	53	48
2	16	78	77
2	17	28	19
3	0	221	209
3	1	172	171
3	2	74	72
3	3	97	92
3	4	207	195
3	5	120	111
3	6	182	175
3	7	81	76
3	8	42	45
3	9	57	53
3	10	115	117
3	11	41	39
3	13	37	30
4	0	53	51
4	2	56	57
4	3	84	86
4	4	73	76
4	5	41	55
4	7	68	64
4	10	46	54
4	12	36	30
5	0	40	37
5	1	71	72
5	2	37	38
5	3	65	61
5	5	54	55
5	7	66	68
6	1	67	73
6	3	34	33
6	4	36	24
6	5	60	60
6	7	73	84
6	9	32	39
6	12	31	17
7	2	50	67
7	8	47	48
7	9	29	39
7	10	30	29
8	0	34	50
K = 3**			
3	0	201	213
3	1	33	32
3	2	138	159
3	3	86	81
3	4	126	126
3	5	103	98
3	6	53	28
3	7	84	98
3	11	86	100
3	12	40	28
3	13	72	82
3	16	28	21
4	0	32	39
4	1	49	60
4	2	101	95
4	3	64	57
4	4	50	57
4	5	34	10
4	6	75	89
4	7	57	59
4	9	42	53
4	10	58	54
4	11	37	31
4	15	31	30
5	1	35	30
5	2	112	114
5	3	32	10
5	4	40	36
5	5	48	55
5	6	56	66
5	7	41	12
5	9	42	43
5	12	32	21
6	1	40	53
6	3	60	53
6	4	55	52
6	5	81	91
6	7	49	52
6	8	34	19
6	10	40	25
7	0	48	68
7	2	62	32
K = 4**			
4	0	91	80
4	1	54	59
4	2	93	94
4	3	63	38
4	6	83	93
4	7	94	72
4	8	38	58
4	12	37	24
4	14	37	33
5	0	96	102
5	1	52	55
5	2	74	78
5	3	101	107
5	4	48	42
5	5	56	57
5	9	31	29
5	10	39	44
6	1	42	44
6	2	44	47
6	5	37	49
K = 5**			
5	0	87	88
5	2	58	62
5	3	41	43
5	4	34	21
5	6	36	38
5	8	35	51
K = 6**			
0	0	43	66

Results and Conclusions

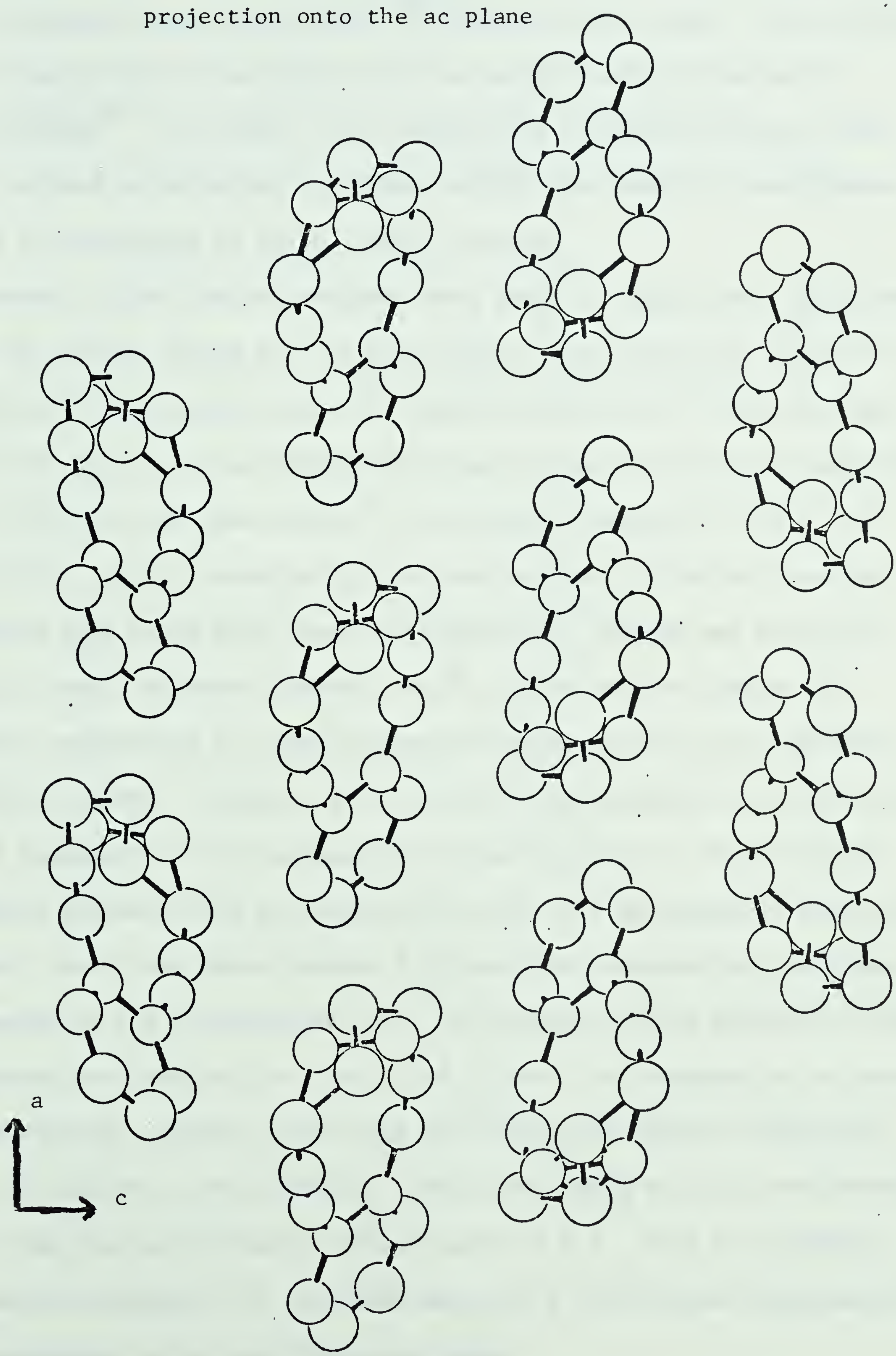
The structural determination shows that the molecular structure is that corresponding to I(b), and the molecule is correctly named 3,4-benzocyclodeca-1,5-diyne. The disorder described earlier limits the precision of the determination and one cannot exclude the possibility that the disorder is even more complicated than assumed and that the crystals contain, for example, a small percentage of I(a). The carbon skeleton is shown in Figure (XXIII), overleaf, with pertinent distances and angles on the diagram. Figure (XXIV) shows the packing of the molecules with the disordered and ordered molecules together, and follows Figure (XXIII).

Figure(XXIII)
A skeletal drawing of 3,4-benzocyclodeca-1,5 diyne seen normal to the best molecular plane.



Figure(XXIV)

A packing diagram of 3,4-benzocyclodeca-1,5 diyne seen in projection onto the ac plane



A detailed discussion of the intramolecular geometry is limited by the systematic errors which must be present in this case. The observed bond lengths are in agreement with the usual literature values for hydrocarbons[24]. The atoms C(2) through C(7) inclusive and their two-fold related carbon atoms are planar within the limits of experimental error as determined in Table (XXXV), overleaf.

Strain within the ten membered ring leads to significant deviations from the normal values for the bond angles. The particular pattern of deviations of the bond angles is somewhat unexpected in that one angle C3-C4-C5, involving the acetylinic link, is considerably more distorted from 180° than the other (166.7° for C3-C4-C5 compared to 174.8° for C2-C3-C4). This is surprising since moving atom C3 further from the two-fold axis would make these two angles more similar and the angle C1-C2-C3 would increase towards 109.5°, the tetrahedral angle. No obvious explanation for this feature of the structure can be advanced.

Table (XXXVI) overleaf, shows important intermolecular contacts with those dependent on the conformation grouped together. The 0.25-0.25 occupied distances are not reported as there are no unusually short distances, other than those between 0.25 occupied positions and positions unchanged by the conformation, i.e. not involved in the disorder. These positions are reported for the 0.75-0.25 case. An examination of these intermolecular contacts shows only one disruptive feature associated with the disorder, the C6-H2d(1) contact of 2.68 Å which is considerably less than the van der Waals contact sum of 2.9 Å. This is presumably the major contributor to the preference for a C1-C1d bond approximately perpendicular to the four-fold screw axis.

Table (XXXV)

Plane defined by atoms C(2) - C(7) and their two-fold related atoms with respect to a cartesian coordinate system.

$$0.445x - 0.445y + 0.777z - 3.5111 = 0$$

Atom	Deviation from plane in Angstroms
C(2)	0.044
C(3)	-0.004
C(4)	-0.002
C(5)	-0.016
C(6)	-0.013
C(7)	-0.034
C(1)	-0.496
C(1d)	0.533

Table (XXXVI)

Intermolecular Distances

All distances in Å

0.75-0.75

Atom 1	Atom 2	Symmetry Position	Distance
H1(2)	H7	x-1, y-1, z	2.48
H1(1)	H6	y, x-1, -z	2.65
H1(1)	H2(1)	½+y, ½-x, ¼+z	2.64
C4	H2(2)	½-x, ½+y, ¼-z	2.87
C5	H2(2)	½-x, ½+y, -¼-z	2.91
C6	H2(1)	1+y, x, -z	2.90

0.75-0.25

Atom 1	Atom 2	Symmetry Position	Distance
$H1_d(1)$	H7	x-1, y-1, z	2.46
$H2_d(1)$	H6	y, x, -1-z	2.49
$H2_d(2)$	H1(1)	½-y, ½+x, z-1	2.60
$H1_d(2)$	H2(1)	½-x, ½+y, ¼-z	2.52
C4	$H1_d(1)$	½-x, ½+y, -¼-z	2.83
C5	$H1_d(1)$	½-x, ½+y, -¼-z	2.84
C6	$H2_d(1)$	1+y, x, -z	2.68
C6	$H1_d(1)$	½-x, ½+y, -¼-z	3.01
C1	C4	½-x, y-½, -¼-z	3.61
C1C	C5	½-x, y-½, -¼-z	3.52
C1	C6	½-x, y-½, -¼-z	3.75

Appendix III

The Programme used to locate the 3,4-benzocyclodeca-1,5-diyne molecule within the unit cell.

```
      REAL X(10), Y(10), SCAT(6), A(6), FO(6), FC(6), TOBY(6),
     1EGX(10), WH1(10), Z(10)
      P=3.1416
      SMITM=0.0
      THET=0.0
      ROOT2=SQRT(2.0)
      DO 1 I=1,7
      READ2,X(1),Y(1)
2     FORMAT(2F10.5)
      EGX(1)=X(1)
      WM1(1)=Y(1)
      Z(1)=0.0
1     CONTINUE
      DO 4 1-1,5
      READ3,SCAT(1)
3     FORMAT(F10.5)
4     CONTINUE
      DO 5 J=1,5
      READ6,FO(J)
6     FORMAT(F10.5)
5     CONTINUE
      SUMFO=0.0
      DO 8 K=1,5
      SUMFO=SUMFO+FO(K)
8     CONTINUE
59    PRINT61,THET
61    FORMAT('1','TILT IS',F5.1,'DEGREES')
      SMITM=0.0
      PRINT 63
63    FORMAT(15X,'X',20X,'Y',20X,'Z')
      DO 65 1=1,7
      PRINT64,1,X(1),Y(1),Z(1)
64    FORMAT(5X,'C',12,2X,3(F10.5,10X)
65    CONTINUE
      PRINT 62
62    FORMAT(5X,'R',10X,'TRANSLATION',80X,'COMMENT')
60    ROY=0.0
      DO 20 1=1,5
      A(1)=0.0
20    CONTINUE
      DO 30 1=1,5
      DO 40 J=1,7
      SUM=8.0*(COS(2.0*P*1*X(J))*COS(2.0*P*1*Y(J)))
      SOM=SCAT(1)*SUM
      A(1)=A(1)+SOM
40    CONTINUE
30    CONTINUE
      DO 70 J=1,5
```

Appendix III continued

```
      FC(J)=ABS(A)(J))
70    CONTINUE
      SUMFC=0.0
      DO 50 1=1,5
      SUMFC=SUMFC+FC(1)
50    CONTINUE
      SCALE=SUMFO/SUMFC
      DO 80 1=1,5
      FC(1)=FC(1)*SCALE
80    CONTINUE
      DO 90 K=1,5
      TOBY(K)=ABS(FO(K)-FC(K))
90    CONTINUE
      ROBBER=0.0
      DO 100 J=1,5
      ROBBER=ROBBER+TOBY(J)
100   CONTINUE
      R=ROBBER*100.0/SUMFO
      IF(R.LT.15)GOTO1000
      PRINT35,R,SMITM,FC(1),FC(2),FC(3),FC(4),FC(5),SCALE
35    FORMAT(1X,F10.5,'  %  ',F10.5,6(F10.5,2X),'THATS NOT
     1 PERFORMANCE.')
      GOTO200
1000  PRINT99,R,SMITM,FC(1),FC(2),FC(3),FC(4),FC(5),SCALE
99    FORMAT(1X,F10.5,'  %  ',F10.5,6(F10.5,2X),'NOW THATS
     1 PERFORMANCE******')
200   SMITM=SMITM+0.025
      IF(SMITM.GT.0.5)GOTO300
      DO 45 J=1,7
      X(J)=X(J)+0.025
      Y(J)=Y(J)+0.025
45    CONTINUE
      GOTO60
300   DO 301 1=1,7
      X(1)=EGX(1)
      Y(1)=WH1(1)
      Z(1)=0.0
301   CONTINUE
      THET=THET+5.0
      THET=THET/57.3
      DO 7 K=1,7
      D=((X(K)-Y(K)))*7.890/ROOT2
      Z(K)=Z(K)+((D*SIN(THET)))/17.1
      CHANGE=(D*(1.0-COS(THET)))/(7.89*ROOT2)
      X(K)=X(K)-CHANGE
      Y(K)=Y(K)+CHANGE
7     CONTINUE
      THET=THET*57.3
      IF(THET.GT.90.0)STOP
      GOTO59
      END
```